The Essential Oils

BY

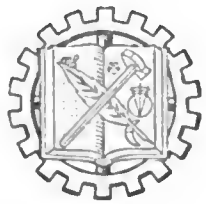
ERNEST GUENTHER, PH.D.

Vice President and Technical Director
Fritzsche Brothers, Inc., New York, N. Y.

VOLUME FIVE

INDIVIDUAL ESSENTIAL OILS OF THE PLANT FAMILIES

ROSACEAE, MYRISTICACEAE, ZINGIBERACEAE, PIPERACEAE, ANACARDIACEAE, SANTALACEAE AND MYOPORACEAE, ZYGOPHYLLACEAE, LEGUMINOSAE, HAMAMELIDACEAE, DIPTEROCARPACEAE, ANONACEAE, OLEACEAE, AMARYLLIDACEAE, RUBIACEAE, MAGNOLIACEAE, CAPRIFOLIACEAE, VIOLACEAE, RESEDACEAE, SAXIFRAGACEAE, CARYOPHYLLACEAE, PRIMULACEAE, TILIACEAE, AND COMPOSITAE



1952

D. VAN NOSTRAND COMPANY, INC.

TORONTO NEW YORK LONDON

NEW YORK
D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York 3
TORONTO
D. Van Nostrand Company (Canada), Ltd., 228 Bloor Street, Toronto
LONDON
Macmillan & Company, Ltd., St. Martin's Street, London, W.C. 2

COPYRIGHT, 1952, BY
D. VAN NOSTRAND COMPANY, INC.

Published simultaneously in Canada by
D. VAN NOSTRAND COMPANY (Canada), LTD.

All Rights Reserved

This book, or any part thereof, may not be reproduced in any form without written permission from the author and the publisher.

PRINTED IN THE UNITED STATES OF AMERICA

Dedicated
to Mr. Frederick H. Leonhardt,
President of
Fritzsche Brothers, Inc.,
whose vision and generosity made this
work possible

PREFACE

The present work, like the two previous volumes of this series, describes the production, physicochemical properties, chemical composition, and uses of *individual* essential oils. For the reason noted in the Prefaces to Volumes III and IV, these oils are grouped within the botanical families to which the corresponding plants belong, but the families themselves are not arranged according to any taxonomic system.

Some of the oils treated in this volume are of great importance to the flavor chemist: nutmeg, cardamom, ginger, pepper, cubeb, star anise—to mention only a few. Others will be of interest to perfume, cosmetic, and soap perfumers: among these are rose, sandalwood, cananga, ylang ylang, jasmine, tuberose, and violet.

Originally it was hoped that the fifth volume would complete the treatment of individual essential oils. In the course of preparation, however, the book grew to such size that division into two parts became necessary. The present volume, therefore, will be followed by a sixth—the last of the series.

ERNEST GUENTHER

New York, N. Y.
January, 1952

NOTE

All temperatures given in this work are expressed in degrees Centigrade unless otherwise specified in the text.

ACKNOWLEDGMENT

In the preparation of this series, it has been the author's practice, where methods of production, physicochemical properties of oils, and questions of quality are discussed, to draw intensively upon his own experience in the essential oil industry. However, as a result of far-reaching political and economic events, such profound changes have occurred recently in this field, that no individual could possibly hope to keep personally abreast of developments without the cooperation of leading producers and experts throughout the world. Fortunately, the author has been able to rely upon personal and business friends, in many countries, as uninterrupted sources of pertinent and up-to-the-minute data. He wishes, therefore, to take this opportunity to express his sincere thanks to these amiable co-workers, and particularly to the following:

Mr. Ramon Bordas, Destilaciones Bordas Chinchurreta, S. A., Sevilla, Spain.

Mr. João Dierberger, Dierberger Agro-Comercial Ltda., São Paulo, Brazil.

Mr. Jean Duclos, Les Fils de Maurice Duclos, Paris, France.

Dr. Teikichi Hiraizumi, Takasago Perfumery Co., Ltd., Tokyo, Japan.

Mr. F. J. Ippisch, Asociacion de Productores de Aceites Esenciales (formerly Oficina Controladora de Aceites Esenciales), Guatemala, C. A.

Mr. G. O. Krauch, F. Krauch & Cia., S. A., Asunción, Paraguay.

Dr. Francesco La Face, Stazione Sperimentale, Reggio Calabria, Italy.

Dr. Karl H. Landes, Karl H. Landes, Inc., New York, N. Y.

Dr. Yves-René Naves, Research Laboratories of Givaudan & Cie., Geneva, Switzerland.

Dr. J. A. Nijholt, Laboratorium Voor Scheikundig Onderzoek, Buitenzorg, Java.

Mr. S. G. Sastry, Government of Mysore Sandal Oil Factory (Retired), Bangalore, India.

Mr. Carlos Schaeuffler, Schaeuffler Hermanos, Retalhuleu, Guatemala, C. A.

Mr. Edwin H. Sennhauser, Volkart Brothers, Inc., New York, N. Y.

Data contained in the monographs on most of the natural flower oils produced in Southern France and Morocco (jasmine, rose, cassie, mimosa, violet, etc.), and on several other essential oils represent the result of years of closest collaboration with the author's esteemed friend, Mr. Pierre Chauvet, of Seillans (Var), France.

With Mr. Robert Garnier, of Paris, the author had the privilege of studying rose oil production over a period of several seasons at the very source—the "Valley of the Roses," in Bulgaria.

Mr. Charles Muller, of Ambanja, Madagascar, initiated the author into the complexities of ylang ylang distillation in Nossi-Bé some years ago, and has continued to be an invaluable informant on the subject up to the latest moment.

Mr. A. R. Penfold and Mr. F. R. Morrison, both of the Museum of Applied Arts and Sciences, Sydney, Australia, wrote the section on Australian Sandalwood Oils. The author is greatly indebted to these leading experts in Australian essential oils for this interesting contribution.

Dr. Theodor Philipp Haas, of the Philadelphia College of Pharmacy and Science, has generously lent his extensive botanical knowledge wherever any question of nomenclature has arisen.

To the Staffs of the Libraries of the Chemists' Club and of the Bronx Botanical Garden, both in New York, the author is grateful for their unfailing courtesy, patience, and efficiency.

As usual, the author has leaned heavily upon his associates at Fritzsche Brothers, Inc., New York—particularly Mr. Edward E. Langenau, Director of Analytical Laboratories, who furnished most of the data on the physicochemical properties of oils examined in the laboratories of Fritzsche Brothers, Inc. Sincere thanks are also due to Mr. W. P. Leidy and Mr. A. H. Hansen, of the Library of the same Company, for their help with every phase of the literature on the subject. And once more, the author must single out for special praise his faithful secretarial staff—Mrs. Ann Blake Hencken, Miss Catherine McGuire, Mrs. Agnes Clancy Melody, and Mrs. Elizabeth Adelmann, who have for so long shared the burden of a complicated manuscript!

ERNEST GUENTHER

CONTENTS

I. ESSENTIAL OILS OF THE PLANT FAMILY *ROSACEAE*

Oil of Rose 3
I. The Bulgarian Rose Oil Industry 6
A. Distilled Rose Oil ("Otto of Rose" or "Attar of Rose") 10
B. Extracted Rose Oil (Concrete and Absolute of Rose) 32
II. The Turkish Rose Oil Industry 35
III. The French Rose Oil Industry 38
A. Distilled Rose Oil 39
B. Extracted Rose Oil (Concrete and Absolute of Rose) 40
IV. The Moroccan Rose Oil Industry 42
V. The Russian Rose Oil Industry 46
Oil of Bitter Almond 48
Oil of Cherry Laurel 54
Oil of *Spiraea Ulmaria* L. 56

II. ESSENTIAL OILS OF THE PLANT FAMILY *MYRISTICACEAE*

Oils of Myristica 59
Oil of Nutmeg and Oil of Mace 59
Oil of *Myristica Fragrans* Houtt., from the Leaves 79
Oil of *Myristica Succedanea* Bl. 80
Oil of *Myristica Argentea* Warb. 80
Oil of *Myristica Malabarica* Lam. 81

III. ESSENTIAL OILS OF THE PLANT FAMILY *ZINGIBERACEAE*

The Cardamom Oils 85
Oil of *Elettaria Cardamomum* Maton var. *Minuscula* Burkhill 85
Oil of *Elettaria Cardamomum* Maton var. *β-Major* Thwaites 99
Oil of *Amomum Cardamomum* L. 101
Oil of *Amomum Globosum* Lour. 102

Oil of *Amomum Aromaticum* Roxb. 103
Oils of *Aframomum Angustifolium* (Sonn.) K. Schum. and *Amomum Korarima* Pereira 103
Oil of *Aframomum Melegueta* (Roscoe) K. Schum. 104
Oil of *Zingiber Nigrum* Gaertn. 105
Oil of Ginger 106
Oleoresin Ginger 118
The Curcuma Oils 120
Oil of *Curcuma Longa* L. 120
Oil of *Curcuma Aromatica* Salisb. 122
Oils of *Curcuma Domestica* Valeton and *Curcuma Xanthorrhiza* Roxb. 123
Oil of *Curcuma Amada* Roxb. 124
Oil of *Curcuma Caesia* Roxb. 125
Oil of *Curcuma Zedoaria* Roscoe (Oil of Zedoary) 125
Oil of Galangal 127
Oil of *Alpinia Galanga* Willd. 129
Oil of *Kaempferia Galanga* L. 130
Concrete and Absolute of Longoze 131

IV. ESSENTIAL OILS OF THE PLANT FAMILY *PIPERACEAE*

Oil of Pepper 135
Oil of Pepper Berries (*Piper nigrum* L.) 135
Oleoresin of Pepper 144
Oil of Pepper Leaves (*Piper nigrum* L.) 146
Oil of Pepper Berries from "Long Pepper" 147
Oil of Cubeb 148
Oils of False Cubebs 155
The Matico Oils 157
Oil of *Piper Angustifolium* Ruiz et Pavon 159
Oil of *Piper Angustifolium* var. *Ossanum* C. DC. 159
Oil of *Piper Camphoriferum* C. DC. 159
Oil of *Piper Lineatum* Ruiz et Pavon 159
Oil of *Piper Acutifolium* Ruiz et Pavon var. *Subverbascifolium* 160
Oil of Betel 160

V. ESSENTIAL OILS OF THE PLANT FAMILY *ANACARDIACEAE*

Oil of *Schinus Molle* L. 165
Oil from the Berries 166
Oil from the Leaves 167

Oil from Leaves and Berries 168
Oil of Mastic (Oil of Mastiche) 169

VI. ESSENTIAL OILS OF THE PLANT FAMILIES *SANTALACEAE* AND *MYOPORACEAE*

Oil of Sandalwood East Indian 173
Sandalwood Oils Australian 187
A. Oil of *Eucarya Spicata* Sprag. et Summ. (West Australian Sandalwood Oil) 187
B. Oil of *Santalum Lanceolatum* R. Br. 191
C. Oil of *Eremophila Mitchelli* Benth. 192
Oil of Sandalwood African (*Osyris* Oil) 193

VII. ESSENTIAL OILS OF THE PLANT FAMILY *ZYGOPHYLLACEAE*

Oil of Guaiac Wood 197

VIII. ESSENTIAL OILS OF THE PLANT FAMILY *LEGUMINOSAE*

Oil of Balsam Copaiba 203
Balsam Copaiba 203
Oil of Copaiba 209
Oil of Balsam Copaiba African 211
Oil of Balsam Peru 212
Balsam Peru 212
Oil of Balsam Peru 217
Oil of Balsam Tolu 220
Balsam Tolu 220
Oil of Balsam Tolu 222
Oil of Cabreuva 225
Concrete and Absolute of Cassie 227
I. *Acacia Farnesiana* 227
II. *Acacia Cavenia* 232
Concrete and Absolute of Mimosa 234
Concrete and Absolute of *Spartium Junceum* L. (Concrete and Absolute of *Genêt*) 237
Concrete and Absolute of *Genista Tinctoria* L. 239
Concrete and Absolute of Lupine 239
Concrete and Absolute of Wistaria 240

IX. ESSENTIAL OILS OF THE PLANT FAMILY *HAMAMELIDACEAE*

Oil of Styrax (Oil of Storax) 243

Digitized by Google Original from CORNELL UNIVERSITY

I. Levant or Asiatic Styrax 243
Oil of Levant or Asiatic Styrax 247
II. American Styrax 249
Oil of American Styrax 253
Oil of *Hamamelis Virginiana* L. (Oil of Witch Hazel) 255

X. ESSENTIAL OILS OF THE PLANT FAMILY *DIPTEROCARPACEAE*

Oil of Gurjun Balsam 259
Oil of Borneocamphor 261

XI. ESSENTIAL OILS OF THE PLANT FAMILY *ANONACEAE*

Oil of Cananga 267
Oil of Ylang Ylang 276
I. Ylang Ylang Oil from Nossi-Bé, Madagascar and the Comoro Islands 279
II. Ylang Ylang Oil from Réunion Island 302
III. Ylang Ylang Oil from the Philippine Islands 305
Concrete and Absolute of Ylang Ylang 312

XII. ESSENTIAL OILS OF THE PLANT FAMILY *OLEACEAE*

Concrete and Absolute of Jasmine 319
Concrete and Absolute of Lilac 338

XIII. ESSENTIAL OILS OF THE PLANT FAMILY *AMARYLLIDACEAE*

Concrete and Absolute of Tuberose 343
Concrete and Absolute of Narcissus 348
Concrete and Absolute of Jonquil 351

XIV. ESSENTIAL OILS OF THE PLANT FAMILY *RUBIACEAE*

Concrete and Absolute of Gardenia 355
Concrete and Absolute of Karo-Karoundé 356

XV. ESSENTIAL OILS OF THE PLANT FAMILY *MAGNOLIACEAE*

Oil of Star Anise 361
A. Oil of Star Anise Fruit 361
B. Oil of Star Anise Leaves 376

Digitized by Google
Original from CORNELL UNIVERSITY

Oil of Star Anise Japanese 378
Concrete and Absolute of Champaca 379
A. Oil of *Michelia Champaca* L. (True Champaca Oil) ... 379
B. Oil of *Michelia Longifolia* Blume 381
C. Commercial So-called Champaca Oils 381
Oil of Magnolia 382
A. Magnolia Flower Oil 382
B. Magnolia Leaf Oil 383

XVI. ESSENTIAL OILS OF THE PLANT FAMILY *CAPRIFOLIACEAE*
Concrete and Absolute of Honeysuckle 387

XVII. ESSENTIAL OILS OF THE PLANT FAMILY *VIOLACEAE*
Concrete and Absolute of Violet 391
A. Concrete and Absolute of Violet Flowers 393
B. Concrete and Absolute of Violet Leaves 396

XVIII. ESSENTIAL OILS OF THE PLANT FAMILY *RESEDACEAE*
Concrete and Absolute of Reseda 401

XIX. ESSENTIAL OILS OF THE PLANT FAMILY *SAXIFRAGACEAE*
Concrete and Absolute of *Philadelphus Coronarius* L. 407

XX. ESSENTIAL OILS OF THE PLANT FAMILY *CARYOPHYLLACEAE*
Concrete and Absolute of Carnation (Carnation Flower Oil) . 411

XXI. ESSENTIAL OILS OF THE PLANT FAMILY *PRIMULACEAE*
Concrete and Absolute of Cyclamen 417

XXII. ESSENTIAL OILS OF THE PLANT FAMILY *TILIACEAE*
Concrete and Absolute of Linden Blossom 421

XXIII. ESSENTIAL OILS OF THE PLANT FAMILY *COMPOSITAE*
Oil of *Achillea Moschata* L. ("Iva Oil") 425

Digitized by Google
Original from CORNELL UNIVERSITY

Oil of Arnica 426
A. Oil of Arnica Flowers 427
B. Oil of Arnica Root 427
Oil of *Artemisia Tridentata* Nutt. (Oil of American Sagebrush) 428
Oil of *Artemisia Vulgaris* L. 430
Oil of *Blumea Balsamifera* DC. 431
Oil of Chamomile (Roman or English Chamomile Oil) 433
Oil of German Chamomile 438
Oil of Costus Root 446
Oil of Davana 451
Oil of Elecampane 453
Oil of Erigeron 456
Oil of Estragon (Oil of Tarragon) 459
Oil of Sweet Goldenrod 464
Oil of *Helichrysum Angustifolium* DC. 467
Concrete and Absolute of *Helichrysum Angustifolium* 470
Oil of *Helichrysum Stoechas* DC. 471
Oil of Milfoil (Oil of Yarrow) 472
Oil of *Santolina Chamaecyparissus* L. 475
Oil of Tagetes 477
Oil of Tansy 480
Oil of Levant Wormseed 485
Oil of Wormwood 487

INDEX 497

Digitized by Google
Original from CORNELL UNIVERSITY

ILLUSTRATIONS

Facing Page

Rose distillation in Bulgaria. A battery of old-fashioned direct fire stills. 46
A modern rose distillery in Bulgaria equipped with direct fire stills..... 46
Separation of the condensate into rose oil and distillation water..... 46
East Indian nutmeg. The whole nutmeg fruit, and cut fruit showing the mace surrounding the shell which encloses the nutmeg..... 47
Nutmeg production in Grenada, B.W.I. Sun-drying of nutmegs on large wooden trays (barbecues). The nutmegs have to be turned over from time to time..... 47
A cardamom plant in Southern India..... 78
A young pepper grove in Banka (Indonesia). The young shoots are supported by poles..... 78
A ginger planting on the Cochin Coast (Southern India). A native holding a ginger plant, showing the rhizome..... 78
Bunches of pepper on the left, and pepper berries on the right side. Lampong (Indonesia)..... 78
Production of sandalwood oil in Mysore State, India. Removal of the bark and sapwood from the heartwood of the sandal tree..... 79
Shredding billets of sandalwood by power-driven rapidly rotating knives 79
Production of sandalwood oil, West Australia. Sandalwood billets stacked up in front of a distillery..... 79
Production of balsam copaiba in the lower Amazon Basin, State of Pará, Brazil. A hole is drilled into the lower part of the trunk, from which the balsam will flow..... 174
Production of balsam Peru in El Salvador, C. A. "Cascara Process": Incisions are made in the trunk of a tree, after it has been scorched with a torch flame..... 174
Balsam Peru, El Salvador, C. A. "Trapo Process": Burlap is hammered into the incisions to absorb the flowing balsam..... 174
Balsam Peru, El Salvador, C. A. "Trapo Process": A bundle of burlap soaked with balsam and removed from the incisions..... 174
Production of cananga oil in the Bantam region of Java (Indonesia). Collection of the flowers with long hooked bamboo poles..... 175
Cananga oil, Bantam region. A small boy climbing into the tree with a long bamboo pole to reach the flowers..... 175
Cananga oil, Cheribon region of Java (Indonesia). The harvesters climb up the tall trees on a sort of bamboo ladder..... 175

Digitized by Google
Original from CORNELL UNIVERSITY

Facing Page

Cananga oil, Cheribon region. A wealthy Chinese broker who purchases the bulk of the oil from the native distillers..... 175
Production of cananga oil in the Bantam region of Java (Indonesia). Primitive direct fire stills serve for the distillation of the flowers..... 206
Cananga oil, Bantam region. View of primitive condensers and oil separators..... 206
Production of ylang ylang oil in Nossi-Bé (Madagascar). A branch of an ylang ylang tree bearing flowers..... 207
Native girls with harvested ylang ylang flowers in baskets (Nossi-Bé)... 207
A large ylang ylang distillery in Nossi-Bé. Native girls carrying the harvested flowers to the distillery in the morning..... 207
Production of ylang ylang oil in Nossi-Bé (Madagascar). Inside view of a large distillery. The still tops are lifted, permitting the charging of the flowers into the stills..... 302
A modern ylang ylang still in Nossi-Bé. The still top can be lifted by a hoist and the still can be tilted for discharging of the exhausted flowers. Note the oil separator beneath the condenser on the left, and the U-shaped pipe conducting the distillation water back into the still for automatic cohobation during distillation of the flowers..... 302
Close-up of an oil separator. Note the clear supernatant layer of oil and the milky distillation water beneath, which has to be returned to the still for automatic cohobation..... 302
Production of ylang ylang oil in Manila, Philippine Islands. Harvesting of the flower material. Because of the great height of the trees, most of the flowers cannot be hand-picked but must be torn off the branches with long poles..... 303
Ylang ylang, Manila. Discharge of the spent flower material from a still 303
Flowers of *Jasminum officinale* var. *grandiflorum*..... 334
Jasmine flower harvest in the Grasse region of Southern France..... 334
Jasmine flower harvest in the Grasse region of Southern France..... 335
An extensive jasmine plantation in Morocco. Note the wires across the field which will serve to support the bushes as they grow higher..... 335
Native children bringing the morning's harvest of jasmine flowers to the centrally located extraction plant near Khémisset (Morocco)..... 335
Close-up of a tuberose plant..... 430
Harvest of tuberose flowers near Khémisset, Morocco..... 430
Branch of a mimosa tree in full bloom..... 430
Production of star anise oil in French Indo-China. A native field distillery near Langson..... 431
Star anise oil, French Indo-China. Two native stills located on the edge of a rice field. The retorts are imbedded in the hearth. The still tops

Digitized by Google Original from CORNELL UNIVERSITY

Facing Page

serve as condensers. Between the two stills are two oil separators arranged in cascade form 431
German chamomile (*Matricaria chamomilla*) growing wild in Farmos, Com. Pest, Hungary 462
A plantation of Roman chamomile (*Anthemis nobilis*) near Deáki (Pozsony County), Hungary 462
Harvest of Roman chamomile (*Anthemis nobilis*) in Belgium 462
Production of oil of wormwood (*Artemisia absinthium*) in southern Michigan. Harvesting of the plant material 463
Oil of wormwood. A field distillery in southern Michigan 463

Digitized by Google
Original from CORNELL UNIVERSITY

CHAPTER I

ESSENTIAL OILS OF THE PLANT FAMILY *ROSACEAE*

Digitized by Google
Original from CORNELL UNIVERSITY

OIL OF ROSE

Essence de Rose *Aceite Esencial Rosa* *Rosenöl* *Oleum Rosarum*

History.—Of all the scents used in perfumery that of the rose is one of the oldest and best known. Since time immemorial poets have been inspired by the delightful aroma of this flower, and historians have given many an account of the methods by which its alluring fragrance can be captured. Earliest mention of distillation of roses occurs perhaps in the "Ayur-Vedas" of Charaka and Susruta,[1] a series of books on the "good life," written in ancient Sanskrit. In the "Iliad," Homer[2] describes how Aphrodite anoints the body of the slain Hector with rose oil (by which Homer probably means a rose-scented ointment). When the classic writers—Dioscorides,[3] for example—speak of "Rose Oil," they undoubtedly refer to fatty oils heavily perfumed with rose. Most probably such pomades were prepared by maceration of rose petals in hot fat. (Small quantities of these *pommades* are still manufactured in the Grasse region of Southern France —cf. Vol. I of the present work, p. 198.) Rose pomades were extremely popular in ancient Rome, being used on many festive occasions.

As regards actual distillation of roses, the first description—aside from the somewhat vague account in the Indian Vedas—is probably that of the Arabian historian Ibn Chaldûn,[4] who reported that in the eighth and ninth centuries rose water was an important article of trade, being exported to India and China. From the tenth to the seventeenth century the rose industry was centered in Persia, particularly in Shiraz, that fabled city of poets and oriental culture. From here the industry gradually spread to India, Arabia, North Africa, and—with the help of the conquering Moors —as far as Spain. Returning crusaders brought the rose from Asia Minor to Southern France.

Legend has it that the Mogul emperor Jehángir[5] in India had the canals of his palace gardens supplied with distilled rose water. One day his con-

[1] Sri Madhusudana-Gupta, "The Susruta," Sanskrit College, Calcutta (1835), 2 Volumes.
[2] "Iliad," Chapter 23, V, 186.
[3] "De Materia Medica Libri Quinque," Editio Kühn-Sprengel (1829), Vol. I, 41, 56, 123; II, 399–404.
[4] "Notices et Extraits des Manuscrits de la Bibliothèque Impériale à Paris," Tome 19 (1862), 364. Istakhri, "Das Buch der Länder," Ed. Mordmann, Hamburg (1754), 73.
[5] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. I, 69. Cf. *ibid.*, 17 and 150.

Digitized by Google Original from CORNELL UNIVERSITY

sort noted a thin, oily membrane on the surface of the water in one of the canals and ordered it collected; this highly aromatic substance she named "Atr-i-Jehángiri." Thus, possibly, began the distillation of roses for their essential oil. However, in view of the very large quantities of rose water produced at that period in Persia and neighboring countries, it appears more likely that the separation of the semisolid rose oil on the surface of distilled rose water had been observed before this, and that rose oil had actually been used for the perfuming of aromatic oils and beauty preparations for some time. Thus, an early reference to distilled rose oil is probably contained in Harib's [6] chronicle of the year 961, written in Cordova, Spain. Italian and German literature [7] of the fifteenth and sixteenth centuries describes several methods for the actual distillation of rose water and rose oil. Nevertheless at this period Persia was still the principal producer of rose water, which was exported on Dutch and Portuguese ships via ports in the Gulf of Persia or via Aden in Arabia.

At the beginning of the seventeenth century the conquering Turks introduced the rose industry into the Balkan countries, particularly to Bulgaria, where plantings were started near the newly founded town of Kazanlik, on the southern slopes of the Balkan Mountains. However, it was only in the nineteenth century that the Bulgarian rose oil industry began to prosper and acquire a leading, indeed an almost monopolistic, position, supplying the world with precious rose oil. This condition prevailed until the end of World War II brought about the most profound political and economic changes; Bulgaria's rose industry has now been nationalized, and production greatly reduced. What may take place behind the "Iron Curtain" in regard to rose oil is not clear at the time of this writing. According to some sources, a new rose industry is being created on the Crimean Peninsula, and in the Caucasus, but no detailed report has become available to the Western World.

Aside from Bulgaria, Anatolia in Turkey has been producing limited quantities of rose oil, but compared with the Bulgarian, the quality of the Turkish oil has in general been quite inferior.

The rose industry of Southern France (Grasse region) began early in the nineteenth century. Since the type of rose grown near Grasse is not particularly suited to the production of volatile (essential) oil of rose by distillation, the flowers are extracted with volatile solvent, yielding the so-called concretes and absolutes of rose (see below).

Attempts to cultivate roses in North Africa for extraction purposes have been made on several occasions, but only partly with favorable results. Lately sizable rose plantations, employing modern agricultural equipment,

[6] R. P. A. Dozy, "Le Calendrier de Cordue de l'année 961," Leyden (1873).
[7] Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. I, 153.

Digitized by Google Original from CORNELL UNIVERSITY

have been established in Morocco; these will be described in a separatc section, below.

For ornamental purposes roses are grown on a very large scale, and in many parts of the world, Texas, Oregon, and California among them. However, such roses are bred and cultivated for appearance rather than for exploitation of their essential oil. On distillation or extraction they give a low yield of oil, and an oil of such different quality [8] that the perfume industry cannot use it to replace the Bulgarian or French products.

Botany.—Of the more than 5,000 varieties of roses known to the horticulturist only a relatively few exhibit a marked fragrance; this fragrance, moreover, differs considerably according to plant variety. Thus, the perfume of some types recalls hyacinth or violet flowers, or musk; that of others may be reminiscent of certain fruits—raspberry, for example. Most of the fragrant roses are hybrids.[9] The aroma referred to by perfumers as rose odor in the more narrow sense is found almost exclusively in the roses belonging to the so-called *Centifolia* group (fam. *Rosaceae*); of these only three are exploited commercially for the isolation of their perfume:

1. *Rosa damascena* Mill. forma *trigintipetala* Dieck,[10] the so-called "Pink Damask Rose." Originally probably unknown in the wild state, and most likely developed horticulturally as a hybrid of *Rosa gallica* L. and *Rosa canina* L., it has now escaped cultivation and can be found growing wild in the Caucasus, in Syria, Morocco, and Andalusia. *Rosa damascena* is very fragrant and contains a relatively large amount of volatile oil, which can be isolated by steam distillation or by extraction with volatile solvents. By far the most important of all perfumery roses, it is planted extensively in Bulgaria, and to a smaller extent in Anatolia (Turkey).

2. *Rosa alba* L. or *Rosa damascena* Mill. var. *alba*, the so-called "White Cottage Rose," contains much less volatile oil than *Rosa damascena*, the oil being also of lower quality. Being considerably hardier and more resistant to unfavorable climatic factors than the pink damask rose, the white cottage rose is grown in Bulgaria as a hedge around the pink roses, and in the higher and colder altitudes where *Rosa damascena* does not flourish. Distillers in Bulgaria object to the white rose as being of inferior quality, but farmers insist on growing it for protection and for marking the boundaries of their fields of pink roses.

3. *Rosa centifolia* L., the so-called "Light Pink Cabbage Rose," is grown extensively in the Grasse region of Southern France, and lately also in North

[8] Sorrels and Ratsek, "A Study of Rose Oil Production in Texas," *Agr. Mech. Coll. Texas, Bull.* No. 84 (1944).

[9] *Perfumery Essential Oil Record, Special Issue* **16** (1925), 283–328.

[10] Tschirch "Handbuch der Pharmacognosie," Vol. II, Part 2, Table XXV. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 802.

Digitized by Google Original from CORNELL UNIVERSITY

Africa (particularly Morocco), where it is known as "Rose de Mai." It contains a good amount of flower oil which, however, cannot economically be isolated by steam distillation. Limited quantities are used for the production of the fragrant rose water so popular in Mediterranean and Latin countries. The bulk of *Rosa centifolia* L. serves for extraction with volatile solvents, which yields concretes and absolutes of rose, one of the most important products of the natural flower oil industry in the Grasse region. Concerning the botanical origin of *Rosa centifolia* L., several theories have been advanced in literature.[11] The plant appears to be closely related to *Rosa damascena* Mill.

I. The Bulgarian Rose Oil Industry

Producing Regions.—As has been pointed out, the cultivation of roses for industrial purposes was introduced to Bulgaria by the conquering Turks several hundred years ago. Centers of production lie to the north of Plovdiv, in the valleys of the Toundja and Struma, both tributaries of the Maritsa River. To the north, these two valleys are bordered by the Central Balkan Mountains, to the south by the Sredna-Gora. Of the two sections, the Struma Valley, with Karlovo as center, is now the more important one; in 1938 about 7,700 acres were under rose here. The Toundja Valley in the east, with Kazanlik as center, is the older of the two "Valleys of the Roses;" in 1938 it counted 3,600 acres of rose fields. These two valleys are not the only rose producing areas in Bulgaria; rose plantings can also be found near some villages located on the southern side of the Sredna-Gora. Bulgaria's rose industry reached its peak in 1916 with a total of 22,000 acres. After World War I it went through a critical period, with a substantial reduction of the acreage. In 1938 rose plantations in Bulgaria totaled about 15,000 acres, planted near 142 villages (Karaivanoff[12]). During the years of world-wide depression many rose growers switched their crops to tobacco and peppermint, which promised better returns. World War II brought a further decline in Bulgaria's rose industry; in 1945 less than 5,700 acres were under rose cultivation.[13]

The roses flourish at the foot of the hills or on the southern slopes of the Balkan Mountains, which protect the plantings from cold north and northeast winds. The altitude here ranges from 900 to 1,500 (or even 2,500) ft. The section lies between the grain fields in the valleys and the mountain forests of the Central Balkan range. The soil consists of fertile gravel,

[11] Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 803.
[12] *Drug Cosmetic Ind.* **42** (1938), 580.
[13] *Am. Perfumer* **48** (June 1946), 49.

Digitized by Google Original from CORNELL UNIVERSITY

limestone, sand and loam, mostly free of acids, well drained and easily permeable to water.

Planting, Cultivating and Harvesting.—As was mentioned in the section on "Botany," two types of rose are cultivated in Bulgaria, viz., *Rosa damascena*, the pink or light red rose, and *Rosa alba*, the white rose. Of these, the former is by far the more important, as it yields a much higher percentage of oil, and an oil of superior quality. It grows on shrubs 4.5 ft. high. The bushes of the white rose are higher and stronger—hence their use as hedgerows for protection of the pink roses. Plantings of white rose are also found in the colder areas of the higher altitudes, where the pink rose does not survive.

Prior to planting, the ground must be well plowed; then parallel ditches, 3.5 ft. deep and 1.5 to 1.75 ft. wide, and 7 to 8 ft. apart, are dug. The earth shoveled up from the ditches is piled in equal amounts on both sides of the ditch. This work should be undertaken in the fall, or not less than two months prior to planting, so that the earth can be exposed to air and moisture sufficiently long for the organic matter to decompose. About the end of February or the beginning of March, a part of the earth piled up along the ditch is shoveled back so that the ditch has now a depth of only 1.5 to 2 ft. (The deeper the bushes are planted, the better they will withstand periods of drought.) The cuttings necessary for planting are procured from an old rose field, usually purchased for this purpose. Cuttings 1 to 2 ft. long are taken from the base of healthy old rose bushes, the upper, green parts being removed. The woody cuttings are placed into the ditches horizontally, in four uninterrupted rows, 2.5 to 3 in. apart. Then a layer of earth (from the piles along the ditches), 2 to 3 in. thick, is placed on top of the cuttings; this is followed by 2 in. of seasoned stable manure. In May the first shoots appear above ground. The soil is then slightly hoed, weeds are removed, and some more earth is shoveled into the ditches and placed around the young plants. During the first year this procedure (hoeing, weeding, and placing of earth around the young plants) has to be repeated at least eight times, preferably after each rainfall. In the second and third year the field must be hoed and plowed five times each year. During the winter the plants are hilled up for protection against frost. After ten years the plantation may show signs of decay; the bushes are then cut down to the ground for rejuvenation. If properly taken care of every ten years, a field may remain productive from thirty to forty years. However, such care requires a great deal of work: weeds must be removed, old branches cut out, and plenty of manure applied.

The first harvest can be gathered in the third year; it amounts to only about 1,500 kg. of flowers per hectare. From then on the quantity increases, reaching as much as 5,000 kg. per hectare at the height of productivity. On

Digitized by Google Original from CORNELL UNIVERSITY

the average, a well-kept rose field yields about 4,000 kg. of flowers per hectare per year. Andreeff [14] reported yields of flowers ranging from 1,200 kg. to 2,000 kg. per hectare, varying with the year and the cultural care given to the field.

Blooming begins in the second half of May and continues for three or four weeks. Obviously, date and duration of the crop depend a great deal upon the weather prevailing in a particular year. Mild and humid weather prolongs the flowering period, increasing at the same time the yield of oil and producing an oil of good quality. During very hot and dry weather the harvest may last only two weeks, and the yield of oil may be lowered due to loss by evaporation. Moreover, the quality of the oil is also affected because the large quantities of roses arriving at the distilleries cannot be worked up immediately and may be left lying on the floor for hours. During this interval they are likely to start fermenting or at least to turn so stale that their aroma suffers gravely.

In general, harvesting begins as soon as the flowers begin to open and continues until all have been picked. Flowers are collected by hand, being nipped off just below the calyx; the work is done by peasants with the help of their families. To the visitor the harvest affords a pretty and picturesque sight, characteristic of the "Valley of the Roses." Gathering of the flowers starts at daybreak and ceases, if possible, at eight or nine in the morning, while the dew is still fresh on the flowers. When collected early in the morning, the roses give a much higher yield of oil than when gathered in the afternoon. At the height of the season or in spells of hot weather, each bush produces so many flowers at the same time that the picking may have to be continued into the afternoon in order to gather all the flowers maturing on that day. Yield and quality of the oil will then be poor.

The harvesters drop the flowers into bags that hold from 25 to 30 kg., and then place them into sacks, which are hauled to the distilleries as soon as possible. Transport is via trucks, ox- or horse-drawn carriages, or the backs of donkeys.

Changes in Bulgaria's Rose Industry.—Before discussing methods of distillation and extraction, it may be of interest to review briefly the changes which Bulgaria's rose industry has undergone during the last fifty years.

Until 1902 all the roses were grown on small holdings, by a great number of individual peasants who also distilled their crops in old-fashioned, and primitive portable stills. According to statistics of the Chamber of Commerce in Plovdiv, there existed at that time 2,798 distilleries, with 13,128 small stills.[15] The small lots of oil thus produced were purchased by a number of well-known exporters, who supplied the world market with bulked

[14] *Ind. parfum.* **1** (1946), 168, footnote.
[15] Karaivanoff, *Drug Cosmetic Ind.* **42** (1938), 580.

Digitized by Google Original from CORNELL UNIVERSITY

lots. Some of these exporters enjoyed international reputations. From 1902 on, a number of exporters started erecting distilleries, equipped with large, modern stills, in which they processed flower material supplied by the small peasant-growers. (Large-scale distillers never succeeded in producing their own flower supply for the simple reason that the peasant, with the help of his family, can grow and harvest the flowers at much lower cost than a large landowner, who is always faced with labor difficulties and wage problems.) This enabled these exporters to offer brands of rose oil of their own production, of unquestionable purity, and of a quality superior to that of the peasant oils. Some of the individual brands became well known throughout Europe and America. In 1904 Charles Garnier, of Paris, constructed a plant for extraction with volatile solvents in Kara Sarli; and after 1919 six other large-scale producers equipped their distilleries also with extraction batteries, thus producing not only distilled rose oil, but also concretes of rose (see below). As a result of this development, Bulgaria's rose industry underwent an intense modernization between 1902 and 1922, new installations gradually replacing the old-fashioned field stills. On the other hand, the peasant-distillers, too, had to organize themselves against the competition of the large-scale producers. For this purpose cooperative societies were founded, to process the flowers in their own stills. Some of these cooperatives installed modern equipment, others worked with the old-fashioned small stills. From 1929 on, the number of cooperatives increased gradually, helping thereby the development of the industry. In 1930, more than 75 per cent of Bulgaria's rose oil was produced by large-scale, individual operators, the balance by cooperatives and small peasant-distillers. The flowers have always been grown by the peasants. At the outbreak of World War II there existed in Bulgaria a number of quite modern plants, equipped with 649 open fire stills (see below), 40 steam stills, and 32 apparatus for extraction with volatile solvents.[16]

About 1929 Bulgaria's rose industry and trade underwent some serious disturbances, caused chiefly by the endeavor of a few large-scale producers and exporters to corner the flower supply. As a result of their speculative actions prices soared to such a height that consumers abroad lost interest in natural rose oil, replacing it in their formulas, at least partly, with low-priced synthetic preparations. As the disorder increased in the most alarming manner, with grave consequences for the producers, the Bulgarian Government entered the picture, and after a careful study of the whole rose industry by competent experts, promulgated a number of decrees and regulations (1932 to 1936), which placed the industry under strict government control. These laws aimed at:

[16] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

1. Establishing a reasonable price for the crop every year, the price being held as constant as possible in order to prevent speculation.

2. Insuring and certifying the purity of the oil. For this purpose the government created the "Banque Agricole et Coöpérative de Bulgarie," whose inspectors supervised actual production in every factory and sealed the oil containers. The entire output of rose oil was placed in a specially built warehouse of the bank. Any handling of the oil and the preparation of foreign orders were carried out in the laboratories of the bank, and in the presence of the parties concerned.[17] Every lot of oil was analyzed.

These were the conditions under which Bulgaria's rose oil industry operated at the outbreak of World War II. When, at the end of the war, Bulgaria became a communist country, all rose oil factories were nationalized and the industry was declared a government monopoly. By a law of May, 1945, a state enterprise, "Bulgarska-rosa," was established for the purpose of producing and marketing rose oil and other by-products. Today this state concern is the sole producer of rose oil in Bulgaria, and owns the up-to-date distilleries in the Valley of the Roses. Moreover, it is the only exporter guaranteeing the absolute purity of all rose oil it produces for the world market. The oil is submitted to stringent chemical tests in the modern laboratories which form one of the important features of the plant. After analysis, the oil is stored in containers called "koncoums" (vases). All containers are sealed with the special seal of the "Bulgarska-rosa" and numbered. Each container is accompanied by a certificate of purity (Behar [18]).

A. Distilled Rose Oil
("Otto of Rose" or "Attar of Rose")

Method of Distillation.

(*a*) *In Old-Fashioned Field Stills.*—As was mentioned above, until about fifty years ago practically all rose oil was produced in small, portable, direct-fire stills operated by peasant-growers and set up in convenient spots adjacent to the fields, or in villages, and near a supply of running water.

These simple and portable apparatus—some are still used, particularly in remote mountain villages—hold from 120 to 150 liters. The retort is wider at the base than at the top. Two handles on the side walls permit lifting of the retort and emptying of the contents after distillation. The top of the still consists of a removable spherical head, the still head, from which a gooseneck or connecting pipe leads through a barrel filled with lukewarm

[17] *Ibid.*
[18] *Perfumery Essential Oil Record* **41** (1950), 248.

Digitized by Google Original from CORNELL UNIVERSITY

water, for cooling of the condensate. (In appearance these stills closely resemble the old-fashioned field stills occasionally employed in the lavender regions of Southern France—see the picture in Vol. I of the present work, p. 112. The shape of the retort, and particularly that of the still head—"Tête de Maure" in French—clearly betrays the Arabian origin of these apparatus.) On the other side of the barrel the condenser tube ends above a glass bottle in which the condensate is collected. The stills are made of copper, tinned on the inside. Placed, usually in a row, on a rough brick hearth, the stills are heated by an open fire beneath each unit, the fire being kindled with wood.

Depending upon their condition (fresh or stale), from 15 to 20 kg. of roses are charged into the retort, and four to five times their weight of water is added. From 20 to 30 liters of water are then distilled over; however, no oil separates from this so-called "First Water" (note, however, that with industrial distillation in modern rose stills such separation does take place—see below). The "First Waters" from several stills are bulked, and 100 liters are placed in one of the empty stills, then very slowly redistilled (cohobated) until 12 liters of "Second Water" have come over. (The residual 88 liters of water remaining in the retort are used for a new flower batch.) The 12 liters of distillate are collected first in a large bottle holding 8 liters, and then in a smaller bottle called "Surier." The latter holds only a little more than 4 liters and is long and slender in shape, without any angular walls to which oil droplets, separating from the water, might adhere. To bring about complete separation of the oil, the "Second Water" in both vessels is kept standing for several hours, at the end of which time the oil can be decanted from the top. This is effected by means of a conical spoon resembling an old-fashioned candle extinguisher. The point of the cone has a small hole through which any water drips off; the rose oil, which is of semisolid consistency, stays in the cone and is transferred into the oil container.

Once distillation is under way, the "Second Waters" (the separated oil having been removed) are combined with the "First Waters" from another still, and redistilled (cohobated). The distillate of the mixed waters yields the above-mentioned "Peasant" rose oil.

As regards the residual water remaining with the exhausted roses in the retort (after the first operation), it is sometimes poured, with the flowers, over a screen, the flowers thus separated then being thrown away. Some distillers return this residual water to the same retort for distillation with a new batch of roses. This practice results in a slightly higher yield of oil—but at the expense of quality. Inorganic substances probably accumulate in the water on repeated use, and raise its boiling point, thus "pushing" distilla-

Digitized by Google Original from CORNELL UNIVERSITY

tion of high boiling compounds which do not readily come over in regular water distillation. On the other hand, products of decomposition also accumulate in the residual water, and on distillation impart an undesirable odor to the distillate. For this reason most of the small producers strongly object to the use of the residual water, although it may increase the yield of oil. If it were employed again and again—which for obvious reasons is never done—the distillation of roses in the above-described manner would represent a closed circle, and nothing would be lost, except a certain amount of water by evaporation.

The yield of oil from the old-fashioned "peasant" stills amounts to 1 kg. per 2,500 to 3,200 kg. of roses—a much higher yield than that obtained in modern stills. The explanation of this paradox will be given later.

(*b*) *In Modern Direct Fire Stills.*—For a better understanding of the difficulties connected with rose distillation two points should be emphasized:

1. The roses cannot be distilled by injecting live steam into the flower charge, because under these circumstances the petals agglutinate to form a compact mass, through which the steam cannot penetrate. To prevent such agglutination, the flowers must float freely in boiling water. In other words, the roses must be processed by water distillation (cf. Vol. I of the present work, pp. 112, 120, and 142). Even under these circumstances the petals have a tendency to form a huge lump which slowly rotates in the boiling water. It has been suggested that the stills be equipped with powerful mechanical stirrers, but such stirrers are expensive and may give mechanical trouble.

2. Rose oil is relatively soluble in water, and only a part separates as oil on distillation of the flowers. The distillation waters must be redistilled (cohobated) in order to obtain the water-soluble portion in oil form. As carried out in Bulgaria, distillation of roses is a clever combination of distillation of the flowers and cohobation of the distillation waters—these latter being used again and again for new flower batches. Only by adhering to this procedure can a normal yield of oil be obtained.

The following description of the methods actually employed is based upon the author's observations in the course of two producing seasons in Bulgaria: [19]

Most of the industrial stills employed today are directly fired (with an open fire beneath each retort), and of 1,000 to 2,000 liters capacity. Re-

[19] Guenther and Garnier, *Am. Perfumer* **25** (June, September, October, and November 1930).

Digitized by Google Original from CORNELL UNIVERSITY

quiring no steam generator with accessory steam and water pipes, they offer the advantages of low initial investment and simplicity of operation, important features in the primitive "Valley of the Roses." The stills are made of copper, heavily tinned inside, and of cylindrical shape. Insulation with bricks or some other suitable material permits even distribution and retention of heat inside of the retort. The still top is provided with a manhole through which the flowers can be charged. A grid a few inches above the bottom of the retort prevents contact of the flower material with the directly fired bottom. On the side, and level with the grid, is another manhole (opened and closed by means of levers) through which the exhausted flowers and the residual water can be quickly discharged after completion of the *flower* distillation. The still is also equipped with a pipe and valve, beneath the grid, which permits drawing off the residual waters when the still is used for cohobation.

Generally, the retorts are charged with flowers up to about 10 in. below the still head. The quantity of roses charged depends upon their condition, fresh flowers taking up much more space than those stored in the distillery for a few hours. Retorts of 1,200 to 1,500 liters capacity—the most popular type—are charged with 150 to 300 kg. of roses; these are then covered with 3 to 4 times their weight of water.

For example: a retort of 1,800 liters is charged with 250 to 300 kg. of roses, and 1,200 liters of water are added. The whole mass is stirred thoroughly. Then the manhole in the still top is closed and the fire started. After about 1½ hr., actual distillation starts; this lasts another 1½ hr.—the entire operation thus requiring 3 hr.

At the beginning, great care must be exercised to keep the fire low, so that actual distillation starts slowly. Otherwise the warm expanding air will blow through the condensers with great velocity and carry along the most volatile, highly aromatic constituents of the rose oil, which under such circumstances cannot be recovered. During the operation the inlet for the cooling water in the condensers must be regulated so that the condensate flows at a temperature of 35° to 40° C. At lower temperatures the oil, which contains a good deal of stearoptene, will solidify in the condenser tubes, and no oil will appear in the Florentine flask (oil separator).

Distillation of the *flowers* which, after a slow start, should proceed at a lively pace, is completed when about 140 liters of water per 250 kg. of flower charge have distilled over. The very small quantity of greenish oil separating in the Florentine flask is called "Direct Oil" or "Surovo Maslo" in Bulgarian; this is drawn off with a pipette and poured in a glass bottle. When the oil has been decanted, the 140 liters of distillation water ("First Water") are pumped into a storage tank and bulked with the "First Waters"

Digitized by Google Original from CORNELL UNIVERSITY

(freed of *separated* oil) of other operations. As soon as enough "First Waters" have been accumulated, they are redistilled (cohobated), as explained below.

The exhausted flowers in the retort, together with the residual water, are discharged and *thrown away.*

The yield of "Direct Oil" obtained on distillation of the *flowers* is very low, because the greater part of the rose oil is dissolved in the distillation water ("First Water"). To isolate this dissolved oil the "First Water" has to be redistilled (cohobated). For this purpose 1,200 liters are pumped into a retort of 1,800 liters capacity, and 140 liters are very slowly and carefully distilled off. During this operation the condenser temperature should be low. The process requires about two and a half hours: one and a half hours for heating of the water, and one hour for actual distillation (cohobation).

The condensate consists of 140 liters of "Second Water" (see below) and a small quantity of "Water Oil," called "Prevarka" in Bulgaria. The "Water Oil" is drawn off with a pipette and added to the "Direct Oil" obtained from the distillation of the *flowers* (see above). Combined, the two oils constitute the rose oil of commerce. The freshly distilled oil is poured into glass bottles and exposed to sunlight for several days. This causes impurities and colloidal matter floating in the oil to precipitate, and water to separate. The clear oil is then carefully decanted, filtered, and stored in the well-known tinned copper containers.

The ratio of "Direct Oil" to "Water Oil" is not constant and depends upon several conditions, including quality of flower material and method of distillation. In general, the complete oil consists of about 25 per cent of "Direct Oil" and 75 per cent of "Water Oil."

As regards the above-mentioned 140 liters of "Second Water," after the oil has been decanted they are pumped into the storage tank holding the "First Waters" (also freed of *separated* oil) and redistilled with them to remove any oil remaining in solution (see above). The residual water left in the retort after the 140 liters of "Second Water" have been distilled off is kept in the retort and used for the distillation of a new batch of roses.

With the qualification noted some pages back, the entire process of rose oil distillation does, after all, represent something of a closed circle. The distillation waters are used over again and again, only the essential oil and the exhausted flowers, together with their residual waters, being eliminated. The reader will find a flow sheet of the whole process on page 16 of the present volume.

(*c*) *In Steam Stills.*—The steam stills employed at present for the distillation of roses in Bulgaria closely resemble the large direct-fire stills, except that they are provided with a steam jacket at the bottom for heating

Digitized by Google Original from CORNELL UNIVERSITY

with indirect steam, and with a steam coil for the injection of live steam into the boiling still contents. As in the case of direct-fire distillation the flowers must be covered with boiling water and freely move in it. The use of direct steam allows for quicker heating of the contents in the retort, and for much better and easier regulation of the temperature, hence of the rate of distillation. At the same time, the rising steam bubbles effect a certain stirring action on the flower mass. Otherwise the methods of operation are the same. The amount of the flower charge may be somewhat larger in steam stills than in directly-fired retorts of the same capacity.

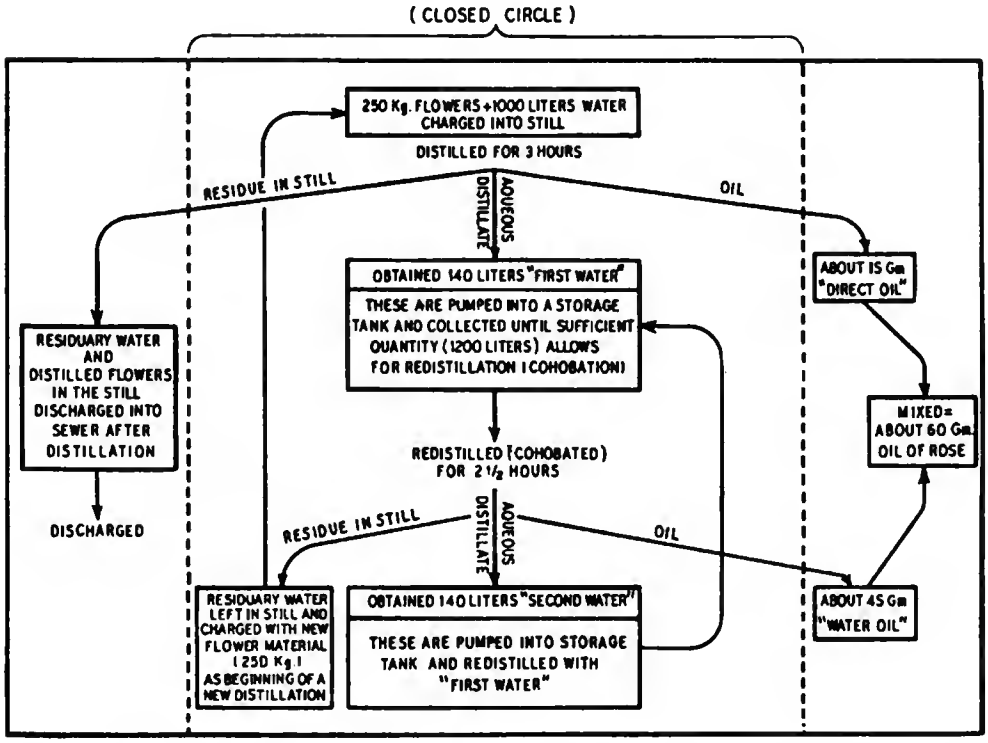
In this connection it should be mentioned that in 1929 one of the leading rose oil producers in Bulgaria modified his rotary extractors (which usually serve for the extraction of roses with volatile solvents—cf. Vol. I of the present work, p. 208) in such a way that they could also be used for distillation purposes.[20] In these apparatus the flowers were charged into metal baskets rotating around a central horizontal axis, and dipping into the solvent at the bottom of the extractor. Instead of a volatile solvent the bottom of the apparatus, in its modified form, contained boiling water heated by injected live steam. The flowers were thus distilled with boiling water and steam. The great advantage of the system consisted in the fact that by the rotary movement of the baskets through the boiling water the flowers were kept moving and prevented from agglutinating. This permitted the use of much less water than the regular stationary retorts. Distillation could be completed in a shorter time, the rate of distillation was greatly increased, and much smaller quantities of "First" and "Second Water" had to be distilled over to yield the totality of oil. The ratio of "Direct Oil" to "Water Oil" was 1 to 2. The complete oil was of excellent quality, and of strong and lasting odor. It contained considerably less stearoptene than the oils produced in the conventional, stationary stills. Unfortunately, production of this type of oil appears to have been discontinued with the outbreak of World War II.

Some years ago another large-scale producer in Rahmanlaré erected a modern distillery equipped with steam stills in which the pressure could be reduced. Distillation in these stills thus represented a modified water distillation at reduced pressure. This process yields oils of very fine odor, free of any "burnt" off-note. The disadvantages lie in the high cost of the solid and airtight apparatus, and in the fact that hydrodistillation at reduced

[20] Since the publication of Vol. I, a new rotary type of extractor has been introduced. This apparatus, constructed by Dumont and Cie., Grasse, A.M., France, is said to offer several advantages over the older types of rotary extractor. It may be used not only for extraction with volatile solvents, but also for hydrodistillation of aromatic plants.

Digitized by Google Original from CORNELL UNIVERSITY

pressure requires large quantities of steam, resulting in an excessive amount of distillation water which tends to dissolve much oil. Cohobation of the distillation waters is therefore a difficult task.



Yield and Quality of Rose Oil.—Yield and quality of the oil depend upon a number of factors, among them the weather, the time of harvest, the condition of the flowers, the type of still used and the method of distillation. The pink *Rosa damascena* yields about twice as much oil as the white *Rosa alba*. The yield is lower at the beginning than at the height of the harvest. In days of mild weather the roses produce much more oil than during spells of intense heat.

On the average, *Rosa damascena* yields 1 kg. of oil per 4,000 kg. of flowers when distilled in industrial stills. Under very favorable conditions only 2,600 kg. of roses may be required per kg. of oil; on the other hand, as much as 8,000 kg. of flowers may sometimes be required to give the same quantity of oil. In directly fired stills the yield is usually slightly higher than in steam stills. In comparative experiments carried out by the author [21] in collaboration with R. Garnier, the yields of oil from flowers of identical origin and quality were:

[21] Guenther and Garnier, *Am. Perfumer* **25** (June, September, October, and November 1930).

Digitized by Google
Original from CORNELL UNIVERSITY

(1) 1:3,890 kg. in a directly-fired still
(2) 1:3,972 kg. in a steam still.

In the old-fashioned, primitive, field stills the yield is substantially higher than in large, industrial apparatus. In these small stills only 2,500 to 3,200 —on the average 3,000—kg. of flowers are required to give 1 kg. of oil. This may appear paradoxical, but the explanation lies in the fact that in the simple peasant stills distillation is "pushed" to the utmost, and often the residual water remaining in the retort with the exhausted flowers is used for the next operation (see above).

Obviously, such "pushing" of the distillation has a marked effect upon the quality of the oil. "Farmer Oils" usually exhibit a weaker odor than the oils obtained in modern large equipment; the odor of the former oils is almost honey-like, sweeter, and less pungent than that of the latter. Of the industrial oils those produced in steam stills have a stronger, more powerful aroma than those distilled in directly fired stills.

The development which has taken place in Bulgaria's rose industry during the past fifty years, viz., the gradual transition from small field stills to large industrial equipment, has not remained without profound changes in the physicochemical properties and chemical composition of the oil itself. The problem, which has caused numerous controversies among prominent essential oil chemists, will be discussed later.

To produce rose oil of highest quality the following principles should be adhered to:

1. The flowers should be collected early in the morning and should be distilled as fresh as possible, without delay.
2. In the retort, the flowers should be covered with water, and well distributed by stirring. Very little excess water should be used.
3. Distillation should be started most carefully and slowly; later it should be maintained at a lively pace. Prolonged action of the boiling water upon the oil is harmful.
4. The volumes of water distilling over should be just sufficient to carry over the oil, but not excessive. Too much aqueous distillate "washes out" the oil separating in the Florentine flask, and redissolves some of its constituents.
5. The temperature of the condenser (and hence that of the flow of the distillate) should be watched carefully.
6. In general, distillation must proceed smoothly, without any "Coups de Feu" (boiling and foaming over).

Physicochemical Properties.—The volatile oil obtained in Bulgaria by distillation of *Rosa damascena* Mill. (often mixed with very small quanti-

Digitized by Google Original from CORNELL UNIVERSITY

ties of *Rosa alba* L.) may be a light yellow, occasionally slightly greenish, mass, semisolid at room temperature. At 16° to 22° C., lanceolate or lamellate, shiny crystals separate from the liquid; because of their low specific gravity, the crystals rise to the surface and cover it with a thin skin which breaks easily if the oil is gently shaken. On cooling, the oil congeals to a transparent soft mass, which can be reliquefied on warming even at hand temperature.

The odor of the oil is powerful and characteristic of fresh roses, the flavor is strong, sweet, and somewhat honey-like.

In 1929 Gildemeister and Hoffmann [22] reported the following properties for Bulgarian rose oil:

Specific Gravity at 20°/15°	0.856 to 0.870
Specific Gravity at 30°/15°	0.849 to 0.862 (The specific gravity decreases with increasing stearoptene content of the oil)
Optical Rotation	−1° to −4°
Refractive Index at 25°	1.452 to 1.466 [23]
Congealing Point	+18° to +23.5°
Acid Number	0.5 to 3
Ester Number	7 to 16
Total Alcohol Content, Calculated as $C_{10}H_{18}O$ (Geraniol)	66 to 75%; in exceptional cases as high as 76%
Citronellol Content (By Formylation—see below)	24 to 37%
Stearoptene Content	17 to 21%
Solubility	Due to its content of sparingly soluble paraffins, rose oil, even in very large quantities of 90% alcohol, gives only turbid mixtures, from which the stearoptene gradually precipitates. The liquid portion of the oil, the so-called "Elaeoptene," is clearly soluble in 70% alcohol

The above properties are those of commercial rose oils produced in Bulgaria prior to 1929. Since then, profound changes in the rose oil industry of that country have taken place (see above): in large part, old-fashioned peasant distillation has been replaced by industrial production, primitive small stills have given way to modern large-scale equipment, and the Bulgarian Government has enforced a strict control over the quality of the oil. Such changes have naturally influenced the physicochemical properties and the chemical composition of the Bulgarian product.

The first deviation from the earlier accepted standards was noted in 1932 by Parry and Seager,[24] who reported that Bulgarian rose oils produced in

[22] "Die Ätherischen Öle," 3d Ed., Vol. II, 821.
[23] Cf. Parry, *Chemist Druggist* **63** (1903), 246. Simmons, *ibid.* **68** (1906), 20.
[24] *Perfumery Essential Oil Record* **24** (1933), 149.

Digitized by Google
Original from CORNELL UNIVERSITY

that year had an exceptionally high citronellol [25] content (45 to 61 per cent against 25 to 40, at the most 45, per cent in the previous thirty years). The ratio of citronellol to geraniol in the oil produced in 1932 was 5.2 to 1, against 0.9–1.25 to 1 in the oils examined in 1930 and 1931. Parry and Seager attributed this change either to special climatic conditions prevailing in 1932 or to adulteration with citronellol. The statement of Parry and Seager was soon afterward challenged by Glichitch and Naves,[26] who asserted that since 1924 they had analyzed a great number of Bulgarian rose oils with a rhodinol (*l*-citronellol) content ranging from 34 to 55 per cent. At about the same time Garnier and Sabetay [27] examined four rose oils distilled in Bulgaria under their supervision and noted the properties given in Table 1.1.

TABLE 1.1

Origin and Method of Distillation	Specific Gravity at 15°	Optical Rotation	Refr. Index at 20°	Melting Point	Ester Number	Ester Number after Acetyl.	Total Alc. Content (%)	Rhodinol Content (%)	Stearoptene Content (%)	Ethyl Alcohol Content (%)
Klissoura, Direct Fire Distillation...	0.8650	−3.48°	1.4630	+17.5°	17.5	228	75.6	46	16	1.4
Kara Sarli, Direct Fire Distillation...	0.863	−4°	1.4585	+20°	8.1	218	71.7	53.7	17.8	3.6
Karlovo, Steam Distillation.....	0.875	−2.40°	1.4582	+17°	6.8	239	80	52	7.3	7.7
Kara Sarli, Rotary Distillation.....	0.8704	−4° 14′	1.4563	+17°	4.5	249	84.2	56.8	8.8	7.2

Garnier and Sabetay thus found that the so-called "Rhodinol (*l*-citronellol) Content," viz., the content of compounds which can be esterified by formylation, was higher than had previously been reported and exceeded 45 per cent. (Note also the relatively high content of ethyl alcohol in some of these oils; for an explanation see below.)

In the same year, C. and R. Garnier [28] more thoroughly investigated the problem of the rhodinol (*l*-citronellol) content in rose oils of various origin and arrived at the conclusion that it ranged from 40 to 63 per cent in oils produced in large modern stills. On the other hand, oils distilled in old-fashioned small stills contained only from 23 to 40 per cent of rhodinol. (The latter compound was determined by hot formylation.) Examining

[25] In the following, the terms *l*-citronellol and *l*-rhodinol will be used interchangeably.
[26] *Parfums France* **11** (1933), 154.
[27] *Compt. rend.* **197** (1933), 1748.
[28] *Bull. soc. chim.* **53** (1933), 513. Cf. R. Garnier, *Perfumery Essential Oil Record* **24** (1933), 370.

Digitized by Google Original from CORNELL UNIVERSITY

various fractions obtained during the distillation of roses in their own factory in Kara Sarli (Bulgaria), C. and R. Garnier [29] observed that the rhodinol content was high in the first fractions and progressively lower in the later fractions. This explains why the earlier rose oils—which were produced chiefly in small peasant stills—contained lesser quantities of rhodinol (*l*-citronellol). In such primitive stills, the quantity of water distilled over is from 1 to 1.5 times greater than the flower charge. In large industrial stills only half the quantity of the water—in relation to the flower charge—is distilled over. Therefore, distillation in small stills gives a better yield of oil than distillation in large, industrial stills. On the other hand, the peasant oils contain less rhodinol (*l*-citronellol) and more inert substances (which weaken the odor) than the industrial oils.

Continuing work on the subject, Garnier and Sabetay [30] in 1934 expressed the opinion that rose oils with less than 40 per cent of rhodinol (*l*-citronellol) should be viewed with suspicion. In some oils of unquestionable purity they observed:

Optical Rotation	−3° 8′ to −3° 44′
Total Alcohol Content, Calculated as Geraniol	67.8 to 89.9%
Apparent Rhodinol Content	41 to 66.4%
Ethyl Alcohol Content	0.9 to 3.35%

In the same year (1934) Glichitch and Naves [31] examined five genuine Bulgarian rose oils (I distilled at Kara Sarli, in rotary apparatus; II at Karlovo, in steam stills; III at Klissoura, in open fire stills; IV at Kara Sarli, in open fire stills; V at Pavel Banya, in open fire stills), and found these properties:

	I	*II*	*III*	*IV*	*V*
Specific Gravity at 25°/15°	0.8630	0.8669	0.8579	0.8548	0.8541
Specific Gravity at 15°/15° (Coefficient 0.0008)	0.8710	0.8749	0.8659	0.8628	0.8621
Optical Rotation	−4° 3′	−2° 33′	−3° 40′	−4° 2′	−3° 33′
Refractive Index at 25°	1.4538	1.4545	1.4603	1.4564	1.4539
Refractive Index at 20° (Coefficient 0.00045)	1.4560	1.4567	1.4625	1.4586	1.4561
Congealing Point	+15.8°	+16.1°	+17.9°	+19°	+17.8°
Acid Number	2.6	3.5	2.6	2.5	2.6
Ester Number	8.7	11.2	10.6	9.8	8.4
Ester Number after Acetylation	243	248.4	224.3	217.7	222.3
Ester Number after Formylation	196.9	185.1	153.9	178.2	188.8
Ester Content, Calculated as $C_{12}H_{20}O_2$	3.04%	3.9%	3.74%	3.42%	2.93%

[29] *Ibid.*
[30] *Ann. fals.* **27** (1934), 264. Cf. *Perfumery Essential Oil Record* **25** (1934), 347.
[31] *Parfums France* **12** (1934), 7.

Digitized by Google
Original from CORNELL UNIVERSITY

	I	II	III	IV	V
Free Alcohol Content, Calculated as $C_{10}H_{18}O$	79.38%	80.04%	70.54%	68.24%	70.49%
Combined Alcohol Content, Calculated as $C_{10}H_{18}O$	2.39%	3.08%	2.91%	2.69%	2.30%
Total Alcohol Content, Calculated as $C_{10}H_{18}O$	81.77%	83.12%	73.45%	70.93%	72.79%
Formylizable Compounds, Calculated as Rhodinol	60.75%	56.75%	46.3%	54.42%	58.0%
Stearoptene Content	8.9%	7.5%	20.2%	20.6%	18.7%

These data led Glichitch and Naves to conclude that Bulgarian rose oils may contain much more than 40 per cent of "Rhodinol" whatever the method of distillation practiced, and in spite of the great variations in content of stearoptenes and total alcohols.

Two years later, Parry [32] published the results of observations on the content of citronellol in rose oils, which he had made in the course of several years:

1. Rose oils remaining liquid even at a low temperature contain more citronellol than oils congealing at a higher temperature (i.e., oils with a higher stearoptene content).
2. Guaranteed pure oils of high citronellol content also have a high content of geraniol, hence a high percentage of total alcohols.

Since the stearoptene content of a rose oil varies with the method of distillation, Parry suggested evaluating the quality of the oil according to the ratio of citronellol to geraniol. Of 28 rose oils examined by Parry and Seager in 1934, only 5 exhibited ratios of citronellol to geraniol higher than 3. In rose oils of high citronellol content, there is a considerable difference in quality between those with a citronellol/geraniol ratio of less than 3, and those with a ratio of about 4 or 5. According to Parry, oils of high citronellol content and a citronellol/geraniol ratio above 3 should be viewed with some suspicion; oils with a ratio of 4 or 5 must be regarded as highly suspect.

In 1938, Karaivanoff,[33] Chief of the laboratories of the "Banque Agricole et Coöpérative de Bulgarie," reported the results of the analyses carried out in this government agency on 243 genuine rose oils distilled in Bulgaria between 1930 and 1937 under the control of government inspectors. The properties of these oils varied within the following limits:

Specific Gravity at 30°	0.848 to 0.8636
Optical Rotation	−2° 12′ to −4° 24′
Refractive Index at 25°	1.4538 to 1.4646

[32] *Perfumery Essential Oil Record* **27** (1936), 278.
[33] *Drug Cosmetic Ind.* **42** (1938), 580.

Digitized by Google Original from CORNELL UNIVERSITY

Congealing Point	+16° to +22.5°
Acid Number	0.93 to 3.08
Ester Number	7.4 to 16.8
Saponification Number	8.4 to 18.7
Ester Number after Acetylation	194 to 240
Rhodinol (*l*-citronellol) Content	27.4 to 56.9%
Stearoptene Content	16 to 24%

(The data quoted by Karaivanoff for "Alcohol Percentage," "Combined Alcohol," and "Free Alcohol" are not included above, because of the unexplained discrepancies that arise when these values are checked against the Ester Number and Ester Number after Acetylation given by Karaivanoff.)

The conclusion of this laboratory was that the content of rhodinol (*l*-citronellol) in pure rose oils ranged from 35 to 51 per cent, the extreme limits being 26.55 and 56.91 per cent. Regarding the difference in the citronellol content of rose oils examined between 1930 and 1937, as compared with that of rose oils produced in previous years, Karaivanoff [34] entirely agrees with the opinions of Poucher,[35] and of C. and R. Garnier (see above), according to which the ratio of "Rhodinol" to geraniol decreases in the successive fractions of distilled rose oils. Since the distillation of the flowers in large industrial stills is not so complete as in small peasant stills, the oils produced in modern equipment contain more rhodinol than those obtained formerly in the primitive small stills. The conclusions of Karaivanoff were affirmed later by Naves [36] who expressed the view that the increase in the rhodinol (citronellol) content was due chiefly to improved methods of distillation, and to the extension of technical supervision to the Bulgarian cooperatives.

The latest data on the physicochemical properties of Bulgarian rose oil are those reported by Behar [37] from the records of the laboratory of "Bulgarska-rosa," which now produces all of the Bulgarian rose oil:

Specific Gravity at 30°	0.8485 to 0.8605
Optical Rotation	−2° 18′ to −4° 24′
Refractive Index at 25°	1.4530 to 1.4640
Freezing Point	+16.5° to +22.5°
Acid Number	0.92 to 3.75
Ester Number	7.2 to 17.2
Saponification Number	8.0 to 20.75
Ester Number after Acetylation	197.87 to 233.33
Free Alcohol Content	62.9 to 75.5%

[34] *Ibid.*
[35] "Perfumes, Cosmetics and Soaps," 6th Ed., Vol. II (1942), 229.
[36] *Mfg. Chemist* **19** (1948), 371.
[37] *Perfumery Essential Oil Record* **41** (1950), 263.

Digitized by Google
Original from CORNELL UNIVERSITY

Combined Alcohol Content.....	2.0 to 4.7%
Total Alcohol Content.....	65.8 to 78.2%
Citronellol Content.....	30.5 to 58.6%
Stearoptene Content.....	18.2 to 21.3%

Another subject of controversy, which attracted the attention of several essential oil chemists over a number of years, revolved about the presence of ethyl alcohol in genuine rose oils. About sixty years ago, Poleck,[38] and Eckart [39] stated that rose oil contains small quantities of ethyl alcohol. Shortly afterward, Schimmel & Co.[40] disputed this, claiming that ethyl alcohol is not a normal constituent of rose oil, but rather an added adulterant, or a product of the partial fermentation that may take place during transport and storage of flowers prior to distillation. If the roses are distilled immediately after harvest, the oil, according to Schimmel & Co., contains no ethyl alcohol.

For many years this view was held to be correct, apparently being substantiated by the fact that pure commercial rose oils (which were then produced chiefly in small peasant stills) contained only traces of (if any) ethyl alcohol. However, in 1933 Garnier and Sabetay [41] reported contents of ethyl alcohol ranging from 1.4 per cent—in genuine oils produced in direct-fire stills—to 7.7 per cent in pure oils distilled in modern steam stills (see above). The findings of Garnier and Sabetay were soon afterward challenged by Parry and Seager,[42] who asserted that, with the exception of rotary-distilled oils, none of the rose oils examined by them contained more than 1 per cent of ethyl alcohol. The latter substance, as well as phenyl ethyl alcohol, can easily be removed by washing the oil three times with hot water. However, oils treated in this manner, and tested by Zeisel's method, still show the presence of ethyl alcohol. This, in the opinion of Parry and Seager, indicates that genuine rose oil contains unidentified compounds with ethoxy, methoxy, or similar groupings, which give the Zeisel reaction and are thus erroneously calculated as ethyl alcohol. (Naves [43] has since demonstrated that the compounds in question are eugenol and its methyl ether.) Continuing work on the content of ethyl alcohol in genuine rose oils, Garnier and Palfray [44] demonstrated that neither

[38] *Ber.* **23** (1890), 3554.
[39] *Ber.* **24** (1891), 4205. Cf. Simmons, *Perfumery Essential Oil Record* **16** (1925), 341.
[40] *Ber. Schimmel & Co.*, October (1892), 36.
[41] *Compt. rend.* **197** (1933), 1748. Cf. *Ann. fals.* **27** (1934), 264. *Perfumery Essential Oil Record* **25** (1934), 347.
[42] *Perfumery Essential Oil Record* **25** (1934), 213.
[43] *Helv. Chim. Acta* **32** (1949), 967.
[44] *Perfumery Essential Oil Record* **26** (1935), 259.

Digitized by Google Original from CORNELL UNIVERSITY

the method of Zeisel,[45] nor that of Thorpe,[46] permits definite conclusions as to the presence and percentage of ethyl alcohol in a rose oil. Distilling 5,000 kg. of freshly harvested roses and carefully cohobating the distillation waters, Garnier and Palfray [47] noted the presence of ethyl alcohol in the distillate and concluded that ethyl alcohol is a normal constituent of fresh roses, 100 kg. of flowers containing at least 0.5 liter of pure alcohol. The actual content of ethyl alcohol in the *oil* depends upon the efficiency of the condenser, the temperature at which the condensate flows, and the construction of the oil separator. In the small primitive peasant stills, in which formerly the bulk of rose oil was produced, the ethyl alcohol was either not condensed at all in the short and warm condenser tube, or "washed out" of the oil by the large quantity of water distilled over. Therefore, "Peasant Oils" contained very little, if any, ethyl alcohol. On the other hand, oils produced in modern stills with efficient condensers do contain a small percentage of ethyl alcohol, the quantity depending chiefly upon the construction of the oil separators. Some of these latter are built in such a way that the separated oil is not "washed out" again by the water distilling over; hence oils obtained in this modern type of equipment may well contain a small quantity of ethyl alcohol.

Whether or not ethyl alcohol should be accepted as a desirable (if normal) constituent of commercial rose oil is another question. It may be argued that ethyl alcohol has no odor value whatsoever, that it acts as a diluent, and that hence it should be removed from the oil before shipment to the market. After all, rose oil is a very high-priced product, and the buyer may well insist upon absence of diluents. If all the ethyl alcohol present in 100 kg. of roses (at least 0.5 liter, according to Garnier—see above) were recovered by efficient condensation, the final product would be a solution of 25 g. of oil (the normal yield from 100 kg. of flowers) in 0.5 liter of alcohol. This certainly could not be considered a "Rose Oil." Nevertheless, ethyl alcohol has come to be considered a normal constituent of rose oil, and very small quantities are now usually admitted in commercial lots.

From the above it can be seen that it is most difficult to establish definite limits for the physicochemical properties of genuine Bulgarian rose oils, since they depend upon many factors—among them soil, altitude, weather, condition (freshness) of the roses, type of apparatus used, method of distillation, and, last but not least, quantity of white roses (*Rosa alba* L.) present in the flower material.

[45] A good description of Zeisel's method can be found in W. W. Scott's "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York (1939), Vol. II, 2527.

[46] For details of the method, see Garnier and Palfray, *Perfumery Essential Oil Record* **26** (1935), 260.

[47] *Perfumery Essential Oil Record* **26** (1935), 259.

Digitized by Google Original from CORNELL UNIVERSITY

As regards these white roses, they yield an oil with a high stearoptene content. Odor and quality are inferior to those of the oil from pink roses (*Rosa damascena* Mill.). In collaboration with R. Garnier, the author [48] distilled *Rosa alba* L. in a modern steam still at Kara Sarli (Bulgaria), and obtained an oil with these properties:

Specific Gravity at 25°	0.8516
Optical Rotation at 25°	−3° 42′
Refractive Index at 25°	1.4569
Congealing Point	+22°
Total Alcohol Content, Calculated as Geraniol	53.35%
Ester Content, Calculated as Geranyl Acetate	3.57%

Guenther and Garnier [49] also studied the influence which fermentation of the flower material exerts upon the quality and properties of the oil. In a series of experiments a batch of freshly picked roses was distilled in a modern steam still immediately upon harvest, another lot was stored for about 12 hr. and then distilled, and a third batch was moistened, kept for two days in an enclosed tank at a temperature of 36° C., and then distilled. The result of storage and fermentation was a marked increase in the specific gravity, a decrease in the congealing point, and, above all, a surprising increase in the ester content of the oils, i.e., from 1.22 per cent in the case of freshly harvested flowers, to 5.74 per cent in the case of stored flowers, and to 46.30 per cent in the case of the fermented flowers. The remarkably high ester content in the oil from the fermented roses was apparently due partly to the formation of phenylethyl acetate, the odor of which was clearly noticeable in the oil.

Analysis and Adulteration.—Being one of the most highly priced essential oils, rose oil has been subject to adulteration since the time it was introduced on the market. Formerly adulteration was carried out in a somewhat crude way—e.g., by the addition of palmarosa oil (which has a high geraniol content), guaiac wood oil, and spermaceti—the latter to simulate a normal stearoptene content in the adulterated oil. Such additions can be detected by careful analysis. Today, however, rose oil is often sophisticated in such a clever way that the analyst may be faced with considerable difficulties. The adulterator now has at his disposal a number of natural isolates from much lower priced essential oils—compounds, moreover, that are also natural constituents of rose oil. The most important of these are geraniol and rhodinol (*l*-citronellol), the latter derived from geranium oil. If added in moderate quantities, these compounds cannot be detected in rose oil by mere

[48] *Am. Perfumer* **25** (December 1930), 621.
[49] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

routine analysis. In such cases, the chemist will have to rely upon careful olfactory tests—which require much training and experience—and upon a thorough chemical examination of the suspected oil. This may be a time-consuming and quite costly procedure.

The following will briefly describe the most important tests developed for the analysis of rose oil, supplementing information given in Vol. I of this work.

Procedures for the determination of specific gravity, optical rotation and refractive index will be found in Vol. I of the present work, pp. 236, 241 and 244, respectively. Because rose oil may be a semisolid mass at room temperature, the *specific gravity* should be measured at 30° C., compared with water at 15° (d_{15}^{30}). The *refractive index* is determined at 30°, the optical rotation at 25°. Note that the *optical rotation* of pure rose oil is low (about −2° to −4° 30′); therefore, moderate additions of geraniol—which is optically inactive—do not influence it much. Palmarosa oil is either slightly dextro- or laevorotatory. The adulterant most commonly used at present, viz., rhodinol (*l*-citronellol) derived from geranium oil, has only a slight effect upon the rotation of rose oil. Nevertheless, even this slight deviation may indicate addition of geranium rhodinol to rose oil (see below). In the opinion of some experts, the higher the laevorotation of a rose oil—within the limits just noted—the better is its quality.

The *congealing point* can be determined by the procedure described in Vol. I of the present work, p. 329. It gives an indication of the stearoptene content of an oil. As has been pointed out in Vol. I, the congealing point of rose oil has been defined as that temperature at which the first crystals appear when the oil is subjected to slow cooling. (This is quite different from the true congealing point of oils such as anise. Cf. Vol. I, p. 253.) Normal rose oils exhibit a congealing point ranging from +18° to +22.5°, the wider limits being +16° to +23° C. Rotary-distilled oils usually have a somewhat lower congealing point than oils produced in direct-fire stills or in steam stills, because the former contain less stearoptene. Oils distilled from white roses (*Rosa alba* L.) are highest in stearoptene, hence exhibit the highest congealing point.

For an assay of the *stearoptene content* and detection of adulterants, see Vol. I of the present work, p. 327. Karaivanoff [50] states that pure Bulgarian rose oils contain from 16 to 24 per cent of stearoptene.

The *ester number* of normal rose oil is low, ranging from about 7 to 17. For determination, see Vol. I, p. 265. Roses that have been slightly fermented prior to distillation yield oils with a much higher ester number than oils from freshly picked flowers (see above).

[50] *Drug Cosmetic Ind.* **42** (1938), 582.

Digitized by Google Original from CORNELL UNIVERSITY

The *total alcohol content* is determined by acetylation (see Vol. I, p. 271) and usually calculated as $C_{10}H_{18}O$, viz., geraniol. According to Karaivanoff, the Ester Number after Acetylation of pure rose oils varies from 194 to 240, which corresponds to a total alcohol content (calculated as geraniol) ranging from 62.4 to 80.5 per cent.[51] The higher the stearoptene content of a genuine rose oil, the lower its total alcohol content. Addition of palmarosa oil—which contains from 75 to 95 per cent of geraniol—usually increases the total alcohol content of a rose oil. The same effect can be obtained by the addition of pure geraniol, or geraniol and citronellol.

The *rhodinol* (*l-citronellol*) *content* of genuine rose oils ranges from 27.4 to 56.9 per cent (Karaivanoff[52]); in rotary-distilled oils it may even be higher, for the reasons explained previously.[53] The rhodinol (*l*-citronellol) content can be determined by formylation (cf. Vol. I of the present work, p. 278). This is a very important assay which should not be neglected whenever a rose oil shows signs of possible adulteration. Two types of citronellol are used today for sophistication of rose oil:

(a) The low-priced citronellol (both *dl*- and *d*-) isolated from sources such as Java citronella oil. Addition of this type of citronellol will markedly decrease the laevorotation of the rose oil.

(b) The higher priced *l*-citronellol isolated from geranium oil. This represents the most annoying form of sophistication now practiced with rose oil. Nevertheless, even such *l*-citronellol can be detected in rose oil, although by a somewhat complex procedure. The method was developed almost twenty years ago by Glichitch and Naves.[54] It is based upon the fact that genuine rose oil contains laevorotatory rhodinol (*l*-citronellol), the rotatory power of which ranges from $-4°$ to $-4° 30'$. It is not possible to obtain an *l*-citronellol of similar high laevorotation economically from any other source. The rotatory power of rhodinol (*l*-citronellol) derived from geranium oil never exceeds $-2° 30'$, and the product from other sources (see above) is either racemic or dextrorotatory.[55] Glichitch and Naves, therefore, recommended isolating the rhodinol (*l*-citronellol) from the suspected rose oil and determining its optical rotation and the dispersion of the latter, after the purity

[51] Author's correction of Karaivanoff's figures for "Alcohol Percentage" (59.6 to 82%). Garnier and Sabetay [*Ann. fals.* **27** (1934), 264. Cf. *Perfumery Essential Oil Record* **25** (1934), 347] reported for genuine rose oil a total alcohol content, calculated as geraniol, ranging from 67.8 to 89.9%.

[52] *Drug Cosmetic Ind.* **42** (1938), 582.

[53] According to Garnier and Sabetay [*Ann. fals.* **27** (1934), 264. Cf. *Perfumery Essential Oil Record* **25** (1934), 347] oils with an apparent rhodinol content of less than 40% should be viewed with suspicion. These authors reported an apparent rhodinol content, in pure oils, ranging from 41 to 66.4%.

[54] *Parfums France* **11** (1933), 156. Cf. Naves, *Mfg. Chemist* **19** (1948), 372.

[55] *Perfumery Essential Oil Record* **37** (1946), 120.

Digitized by Google Original from CORNELL UNIVERSITY

of the isolated *l*-citronellol has been checked by measurement of other properties, among them specific gravity, refractive index, and dispersion of the latter. The rhodinol can be isolated from rose oil by means of the technique developed by Barbier and Bouveault [56] in 1896. In the procedure, the rose oil is heated to 140°–160° in the presence of an excess of benzoyl chloride. All the alcoholic constituents are thereby destroyed, with the exception of the rhodinol (*l*-citronellol) and a part of the phenylethyl alcohol, these two compounds being converted into their benzoic esters. The low boiling products are then eliminated by distillation, and the residue is saponified. The alcohols are subsequently rectified by entrainment with steam, the phenyl ethyl alcohol is destroyed by heating at 140° over potassium hydroxide, according to the procedure of D. Sonntag,[57] and the rhodinol (*l*-citronellol) isolated by fractional distillation. Addition of rhodinol (*l*-citronellol) from any source other than rose oil depresses its rotatory power.

The quantity of *ethyl alcohol* present in a rose oil can be determined by the tests described in Vol. I of the present work, p. 339. As has been pointed out, pure rose oils should contain only a small percentage of ethyl alcohol.

As regards several other specific adulterants of rose oil:

Small quantities of *phenylethyl alcohol* are occasionally added. According to Garnier and Sabetay,[58] this compound has a tendency to increase the congealing point and the apparent rhodinol content of the oil (see above).

Oil of guaiac wood is an old adulterant of rose oil; it has a soft odor reminiscent of tea roses. Moderate additions may result in an increase of the specific gravity, a slight increase in the laevorotation of the rose oil, and a decrease in the total alcohol content. The presence of guaiac wood oil can be detected by isolation of its chief constituent, guaiol m. 91°–93°. The oil leaves a resinous evaporation residue and increases the congealing point of the rose oil. For detection, see also Vol. I of the present work, p. 328.

Oil of Geranium macrorrhizum L., the so-called "Zdravetz Oil," produced in Bulgaria, has occasionally been used for adulteration of rose oil, particularly by small producers who distilled the "Zdravetz Oil" specifically for this purpose.[59] For physicochemical properties of this oil, see Vol. IV of the present work, p. 734.

There are a number of other compounds, small quantities of which occur naturally in rose oil, but which are readily available from other sources and can, therefore, be used as adulterants in conjunction with the above-named products. Among these are *l*-linaloöl, nerol, citral, eugenol, methyl-

[56] *Compt. rend.* **122** (1896), 530.
[57] Mme. de Dortan-Sonntag. Thèse de Doctorat, Faculté des Sciences, Paris (1933). Cf. Sabetay, *Bull. soc. chim.* **45** (1929), 69. Fourneau and Puyal, *ibid.* **31** (1922), 424.
[58] *Ann. fals.* **27** (1934), 264. Cf. *Perfumery Essential Oil Record* **25** (1934), 347.
[59] A. Zlatarov, "La Rose et l'Industrie de l'Essence de Roses en Bulgarie," Sofia (1926).

Digitized by Google
Original from CORNELL UNIVERSITY

eugenol, nonyl aldehyde, and farnesol. If added in traces only, these can hardly be detected.

All of the above proves that oil of rose is strictly an article of confidence and should be purchased only from the most reliable dealers.

Chemical Composition.—The early examinations of rose oil by de Saussure,[60] Blanchet,[61] Baur [62] and Gladstone [63] dealt chiefly with stearoptene and "Elaeoptene"; since the results were vague and inconclusive, they require no discussion in these pages.

The first thorough and fruitful investigation of the main constituent of rose oil is that of Eckart,[64] who in 1890 isolated an alcohol (similar to geraniol) which he named "Rhodinol." (The compound described by Eckart appears actually to have been a mixture of geraniol and *l*-citronellol.) In 1893, Markovnikov and Reformatski [65] isolated a compound "Roseol," to which they assigned the empirical molecular formula $C_{10}H_{20}O$, at the same time claiming it to be the chief constituent of rose oil. Simultaneously, Barbier [66] concluded that the formula $C_{10}H_{18}O$ originally proposed by Eckart was correct. The discrepancies in the results obtained by the above-named researchers induced Bertram and Gildemeister [67] to investigate the chemical composition of rose oil more closely. Examining oils distilled in Bulgaria and Germany, they arrived at the conclusion that the principal component is geraniol, an alcohol $C_{10}H_{18}O$ discovered by Jacobsen [68] in palmarosa oil as far back as 1870, and that the "Rhodinol" of Eckart was only an impure geraniol. In the same year in which Bertram and Gildemeister published their findings, Hesse [69] expressed the opinion that his "Reuniol" (an alcohol $C_{10}H_{20}O$ he had found in geranium oils) occurs probably also in rose oil. Two years later, Tiemann and Schmidt [70] proved the identity of Hesse's "Reuniol" with citronellol obtained by reduction of citronellal. The problem of the identity of "Rhodinol" led to a lively controversy among some of the most brilliant terpene chemists for several decades after 1890. (For details see the original literature,[71] and Vol. II of the

[60] *Ann. chim. phys.* [2], **13** (1820), 337.
[61] *Liebigs Ann.* **7** (1833), 154.
[62] *Neues Jahrb. Pharm.* **27** (1867), 1; **28** (1867), 193. *Jahresber. Pharm.* (1867), 350. *Dinglers polytech. J.* **204** (1872), 253.
[63] *J. Chem. Soc.* **25** (1872), 12. *Pharm. J.* [3], **2** (1872), 747.
[64] *Arch. Pharm.* **229** (1891), 355. *Ber.* **24** (1891), 4205. Cf. Poleck, *Ber.* **23** (1890), 3554.
[65] *J. prakt. Chem.* [2], **48** (1893), 293. *Ber.* **23** (1890), 3191; **27** (1894), 625 Ref.
[66] *Compt. rend.* **117** (1893), 177. Cf. Tiemann and Semmler, *Ber.* **26** (1893), 2708.
[67] *J. prakt. Chem.* [2], **49** (1894), 185.
[68] *Liebigs Ann.* **157** (1871), 232.
[69] *J. prakt. chem.* [2], **50** (1894), 472.
[70] *Ber.* **29** (1896), 903, 922; **30** (1897), 33.
[71] Erdmann and Huth, *J. prakt. Chem.* [2], **53** (1896), 42. Bertram and Gildemeister, *ibid.*, 225. Hesse, *ibid.*, 238. Erdmann and Erdmann, *ibid.* [2], **56** (1897), 1. Bertram and Gildemeister, *ibid.*, 506. Poleck, *ibid.*, 515. *Ber.* **31** (1898), 29. Bertram

Digitized by Google Original from CORNELL UNIVERSITY

present work, p. 178.) Today rhodinol [72] is generally considered to be *l*-citronellol, the latter consisting of a mixture of two isomeric forms in which, according to Doeuvre,[73] the terpinolene or "*β*"-form (isopropylidene form) largely predominates. Studying the infrared spectra of 25 purified acyclic monoterpene compounds, with particular reference to the position and configuration of the double bonds, Barnard, Bateman, Harding, Koch, Sheppard and Sutherland [74] recently obtained very strong evidence that naturally occurring acyclic monoterpenes as a class possess the homogeneous isopropylidene end-group structure. In every purified sample, citronellol (rhodinol) among them, examined by these authors, the proportion of the compound in the isopropenyl form never exceeded 3 per cent and was usually very much less or possibly nil.

In addition to rhodinol (*l*-citronellol) and geraniol, the two principal constituents of rose oil obtained by hydrodistillation of roses, a number of other components have been identified; all constituents are listed below, according to approximate importance:

l-Citronellol. The quantity of *l*-citronellol occurring in rose oil depends chiefly upon the method of distillation (cf. above and "Physicochemical Properties"). Some experts evaluate a rose oil according to its rhodinol (*l*-citronellol) content, claiming that a high rhodinol percentage indicates a very good quality.

Geraniol. The next most important constituent of the oil.

Nerol. According to von Soden and Treff,[75] oil of rose contains from 5 to 10 per cent of nerol, which has a marked influence upon its odor. Von Soden and Treff identified nerol by means of its diphenylurethane m. 52°–53°.

l-Linaloöl. Schimmel & Co.[76] characterized this alcohol by oxidation to citral (naphthocinchoninic acid compound m. 197°–199°).

Phenylethyl Alcohol. Identified simultaneously, but independently, by von Soden and Rojahn,[77] and by Walbaum.[78] Because of its relatively good solubility in water,

and Gildemeister, *ibid.*, 749. See also Barbier, *Compt. rend.* **117** (1893), 177; Monnet and Barbier, *ibid.*, 1092; Barbier and Bouveault, *ibid.* **118** (1894), 1154; **119** (1894), 281, 334; **122** (1896), 530, 673. Bouveault, *Bull. soc. chim.* [3], **23** (1900), 458. Bouveault and Gourmand, *Compt. rend.* **138** (1904), 1699. Cf. Barbier and Bouveault, *ibid.* **122** (1896), 737. Wallach and Naschold, *Nachr. Ges. Wiss. Göttingen* (1896), Meeting February 8th. *Chem. Zentr.* (1896), I, 809. Bertram and Gildemeister, *J. prakt. Chem.* [2], **49** (1894), 185. Cf. *Ber. Schimmel & Co.*, October (1894), 23; April (1895), 37. Barbier and Locquin, *Compt. rend.* **157** (1913), 1114.

[72] The term rhodinol used in its scientific sense, and not to be confused with commercial rhodinol. The latter is usually a mixture of *l*-citronellol, geraniol, and small quantity of other alcohols. Cf. Vol. IV of the present work, p. 701.

[73] *Parfums France* **12** (1934), 197.

[74] *J. Chem. Soc.* (1950), 915. Cf. Naves, *Perf. Ess. Oil Rec.* **43** (1951), 294.

[75] *Ber.* **37** (1904), 1094.

[76] *Ber. Schimmel & Co.*, October (1900), 57.

[77] *Ber.* **33** (1900), 1720.

[78] *Ibid.*, 1903, 2299. Walbaum and Stephan, *ibid.*, 2302.

Digitized by Google Original from CORNELL UNIVERSITY

phenylethyl alcohol occurs in *distilled* rose oil only in small quantities (about 1 per cent). However, the extracted products—concretes and absolutes of rose—contain large quantities of phenylethyl alcohol (see below). In the oil extracted from (distilled) rose water von Soden and Rojahn [79] found 35 per cent of phenylethyl alcohol, and in the volatile oil distilled from rose pomades about 46 per cent. The same authors noted the presence of phenylethyl alcohol also in the residual waters remaining after distillation of the flowers. That phenylethyl alcohol (and eugenol—see below) are actually present in the residual waters, was later confirmed by Guenther and Garnier,[80] in collaboration with Walbaum and Rosenthal.

Farnesol. Reported a constituent of the distilled oil by von Soden and Treff.[81]

Esters. The above-named alcohols occur in the oil chiefly in free form, and to a small degree in esterified form, the ester content (calculated as geranyl acetate) ranging from about 2.5 to 6.0 per cent. These esters are very important as regards the odor of the oil.

Nonyl Aldehyde and Other Higher Aldehydes(?). Schimmel & Co.[82] identified nonyl aldehyde in the oil by oxidation to pelargonic acid m. 252°–253°. This aldehyde, which is probably accompanied by lower and higher homologues, exerts a considerable influence upon the odor of the oil.

Citral. In the course of the same investigation, Schimmel & Co.[83] also noted the presence of citral in rose oil. It was identified by preparation of the naphthocinchoninic acid compound m. 197°–199°.

Eugenol. Von Soden and Treff [84] first found that rose oil contains about 1 per cent of eugenol. This was later confirmed by Naves.[85] Guenther and Garnier [86] observed the presence of eugenol in the residual waters remaining after distillation of the flowers (see above—"Phenylethyl Alcohol").

Eugenol Methyl Ether. Naves [87] recently noted that rose oil contains from 1 to 1.2 per cent of methyleugenol.

Carvone. The same author [88] also reported traces of carvone in the oil.

Sesquiterpenes(?). Investigating genuine Bulgarian rose oils, Garnier and Sabetay [89] observed that they contained small quantities of azulenogenic sesquiterpenes. Like the stearoptene, these sesquiterpenes are insoluble in 75 per cent alcohol, hence they appear as "Stearoptene" in the isolation and assay of the latter by means of 75 per cent alcohol.

[79] *Ibid.* **33** (1900), 1720, 3063; **34** (1901), 2803.
[80] *Am. Perfumer* **25** (December 1930), 621.
[81] *Ber.* **37** (1904), 1094.
[82] *Ber. Schimmel & Co.*, October (1900), 57.
[83] *Ibid.*
[84] *Ber.* **37** (1904), 1094.
[85] *Helv. Chim. Acta* **32** (1949), 967.
[86] *Am. Perfumer* **25** (December 1930), 621.
[87] *Helv. Chim. Acta* **32** (1949), 967.
[88] *Ibid.*
[89] *Ann. fals.* **28** (1935), 585.

Digitized by Google Original from CORNELL UNIVERSITY

Stearoptene. According to Flückiger,[90] the stearoptene present in rose oil consists not of one, but of at least two homologues of the paraffin series C_nH_{2n+2}, because it can be separated into two fractions m. 22°, and m. 40°–41° (cf. Vol. I of the present work, p. 328).

Aside from the constituents described above, oil of rose undoubtedly contains still other substances which play a most important role in the total odor of the oil. Any attempt to compound a synthetic rose oil by using only the constituents just enumerated, and according to the proportions established in natural rose oil, results only in mixtures which exhibit some similarity to the natural product, but which as regards odor are still unsatisfactory. The so-called trace compounds, to which natural rose oil owes its characteristic and powerful odor, occur in it only in minute quantities. They have not yet been identified; or at least nothing definite has been published about their nature. Some years ago, Garnier and Sabetay [91] reported that a small, strongly dextrorotatory fraction occurring between the ethyl alcohol fraction and the rhodinol-geraniol fraction appears to be particularly important as regards the odor of the oil.

In this connection it should also be mentioned that the odor of the distilled rose oil differs greatly from that of the extracted rose products (concretes and absolutes—see below). This difference is caused not only by the large quantity of natural waxes present in the latter products, but also by the occurrence, in the concretes and absolutes, of compounds—particularly phenylethyl alcohol and eugenol—which on distillation of the roses remain mostly in the residual waters, and are thrown away—hence are present in the distilled oil in very small quantities only.

B. Extracted Rose Oil
(Concrete and Absolute of Rose)

The odorous principles present in rose flowers can be isolated more efficiently and completely by the modern method of extraction with volatile solvents (usually petroleum ether) than by hydrodistillation. The so-called concretes and absolutes of rose thus obtained have come to play a very important role in the art of the perfumer, and today the quantity of rose concretes produced largely exceeds that of the distilled oil. Principal areas of production of the concrete are now the Grasse region of Southern France and, to a much smaller extent, Morocco. In these countries *Rosa centifolia* L. is used exclusively; it does not lend itself advantageously to hydrodistillation because it gives only a small yield of distilled oil. The Bul-

[90] *Pharm. J.* [2], **10** (1869), 147. *Z. Chem.* **13** (1870), 126. *Jahresber. Chem.* (1870), 863. "Pharmakognosie," 3d Ed., 170.
[91] *Compt. rend.* **197** (1933), 1748.

Digitized by Google
Original from CORNELL UNIVERSITY

garian roses (*Rosa damascena* Mill. and *R. alba* L.), on the other hand, can be processed either by hydrodistillation or by extraction with solvents. For details of the extraction process itself the reader is referred to Vol. I of the present work, pp. 200 ff.

The solvent extraction process was introduced to Bulgaria by Charles Garnier, who in 1904 erected a plant in Kara Sarli, equipped with a battery of six rotary extractors. In the next thirty years other large-scale rose oil producers followed his example, and in 1938 there were in Bulgaria altogether 32 apparatus [92] for extraction of roses with solvents.

According to trade reports,[93] the following quantities of distilled rose oil and rose concrete were produced in Bulgaria between 1938 and 1945:

Year	*Distilled Rose Oil (in kg.)*	*Concrete of Rose (in kg.)*
1938.....	1,720	2,313
1939.....	3,779	86
1940.....	1,848	2,104
1941.....	836	1,205
1942.....	271	1,268
1943.....	1,133	2,016
1944.....	734	...
1945.....	351	...
1946 [94].....	794	...

From these figures it appears that at times the quantities of rose concrete supplied by Bulgaria exceeded those of the distilled oil. In recent years, however, production of the concrete seems to have been curtailed, owing perhaps to political and economic developments in that country.

Yield and Physicochemical Properties.—According to the author's experience in Bulgaria, from 400 to 450 kg. of *Rosa damascena* Mill. are required to yield 1 kg. of rose concrete which, in turn, gives about 520 g. of alcohol-soluble absolute. Naves and Mazuyer [95] reported yields of concrete (petroleum ether as solvent) ranging from 0.22 to 0.25 per cent. The concrete gives from 50 to 60 per cent of absolute, and contains from 35 to 41 per cent of steam-volatile oil. (The latter is not produced commercially, but only in the laboratory to test the purity of a concrete or absolute—cf. Vol. I of the present work, p. 215.)

[92] Karaivanoff, *Drug Cosmetic Ind.* **42** (1938), 582.
[93] *Annual Rept. Schimmel & Co., Inc., New York* (1950), 50.
[94] Private communication from Mr. T. W. Delahanty, Chief, Consumers Merchandise Branch, U. S. Department of Commerce, Washington, D. C. According to the same source, Bulgaria's rose acreage in 1946 was 6,943 acres, a slight increase over the acreage in 1945 (5,700 acres)—see above. In 1948, production of rose oil in Bulgaria was less than 800 kg.
[95] "Les Parfums Naturels," Paris (1939), 269.

Digitized by Google Original from CORNELL UNIVERSITY

Concrete of rose produced in Bulgaria by extraction with petroleum ether is a light to dark brown waxy mass with a characteristic rose odor, only partly soluble in high-proof alcohol. Walbaum and Rosenthal [96] indicated these properties for Bulgarian rose concrete:

Congealing Point..... +41° to +46.5°, average +44.4°
Acid Number..... 31 to 56

These authors pointed out that the commercial products frequently contain petroleum ether, which has not been completely removed by careful purification and which lowers the congealing point of the concrete. Thus a congealing point of 44.5° in a pure concrete is lowered to 41.5° by the presence of 3 per cent of petroleum ether, to 37° by 15 per cent, and to 34° by 25 per cent of petroleum ether.

As regards the Bulgarian *absolute* of rose, it is a viscous greenish-brown liquid, soluble in high-proof alcohol. Its odor is strong and characteristic of rose, softer, more mellow, and much more lasting than that of the distilled oil.

Schimmel & Co.[97] (I to III), and Naves [98] (IV to VI) reported the following properties for Bulgarian rose absolutes:

	Specific Gravity at 15°	*Optical Rotation* *	*Refractive Index at 20°*	*Acid Number*	*Ester Number*	*Ester Number after Acetylation*	*Total Alcohol Content, Calculated as Geraniol*
I.....	0.9729	+13° 10′	1.50808	9.3	29.9	217.5	71.5%
II.....	0.9682	+14° 25′	1.50633	9.3	30.9	211.9	69.3%
III.....	0.9916	+14° 20′	1.51566	11.2	27.1	218.4	71.8%
IV.....	0.983	+9° 40′	1.5078	4.8	22.4	216.1	70.9%
V.....	0.991	+10° 24′	1.5072	3.5	19.6	243.2	81.8%
VI.....	0.973	+11° 10′	1.5081	4.34	23.1	231.7	77.0%

* Because of their dark color, Schimmel & Co. determined the optical rotation of the absolutes in alcoholic solution.

Note that the Bulgarian rose absolutes exhibit a pronounced dextrorotation, whereas all distilled rose oils are laevorotatory. The compounds causing the dextrorotation in the absolutes are nonvolatile, as is proved by the fact that the volatile oils distilled in the laboratory from the absolutes are laevorotatory (see below).

As was mentioned above, the concrete and absolute contain a certain per-

[96] *Ber. Schimmel & Co., Jubiläums-Ausgabe* (1929), 192.
[97] *Ber. Schimmel & Co.* (1926), 104.
[98] "Les Parfums Naturels," Paris (1939), 270.

Digitized by Google
Original from CORNELL UNIVERSITY

centage of volatile oil which is occasionally isolated in order to determine its physicochemical properties and thereby check the purity of the concretes and absolutes. The properties of seven volatile rose oils thus obtained, and described by Naves and Mazuyer [99] varied within these limits: [100]

Specific Gravity at 15°	0.948 to 0.992
Optical Rotation	−0° 54′ to −2° 42′
Refractive Index at 20°	1.5046 to 1.5190
Acid Number	2.1 to 5.1
Ester Number	5.6 to 10.4
Ester Number after Acetylation	278.6 to 320.6

Chemical Composition.—The volatile oil present in the concrete and absolute of rose probably contains the same constituents as the distilled oil of rose, but in different proportions. Exact data on the Bulgarian concrete and absolute of rose are scarce, because they have not been investigated as thoroughly as the distilled oil (see above). Phenylethyl alcohol, a minor constituent of the oil obtained by hydrodistillation of the flowers, is a very important component of the extracted products. Glichitch and Naves [101] submitted a Bulgarian concrete of rose to steam distillation at reduced pressure, and obtained a volatile oil which consisted of:

Phenylethyl Alcohol	63.7%
Citronellol	22.1%
Geraniol + Nerol	13.7%
	99.5%

Naves [102] reported that concrete of rose also contains small quantities of *eugenol, eugenol acetate,* and traces of a ketone with a minty odor.

II. The Turkish Rose Oil Industry

Roses have been cultivated in Asia Minor for a long time. Before the turn of the century they were used for the distillation of fragrant rose water popular in the Near East as a flavorant in confectioneries, as a medicine, and as a cosmetic. The Turkish rose *oil* industry is said to have had its beginning [103] in 1894 when a Bulgarian peasant of Turkish descent came to Turkey and planted cuttings of *Rosa damascena* Mill., which he had pro-

[99] *Ibid.* Cf. Naves, Sabetay and Palfray, *Perfumery Essential Oil Record* **28** (1937), 336. Glichitch and Naves, *Parfums France* **11** (1933), 163.

[100] The concretes and absolutes investigated had been obtained by extraction with petroleum ether (not benzene).

[101] *Parfums France* **11** (1933), 163.

[102] "Les Parfums Naturels," Paris (1939), 271.

[103] *Ber. Schimmel & Co.* (1917), 45; (1926), 267. Cf. Jeancard, *Perfumery Essential Oil Record* **11** (1920), 210.

Digitized by Google Original from CORNELL UNIVERSITY

cured in Kazanlik and smuggled out of Bulgaria. Encouraged by the Turkish Government he showed the peasants of Anatolia how to produce rose oil in the type of primitive small field stills used at that time in Bulgaria. From this modest start there developed the Turkish rose oil industry which, in the years prior to World War I, attained considerable importance, up to 800 kg. of rose oil being produced yearly at that time. World War I, the ensuing Greco-Turkish War, and the expulsion of the Greeks and Armenians from Anatolia caused a temporary decline in the agricultural and horticultural activities of that part of Turkey, and the rose fields in particular were seriously neglected. Gradually, however, and with the aid of the Turkish Government, the rose industry recuperated, and in the period between the two World Wars, Turkey came to produce from about 100 to 300 kg. of rose oil per year.

The producing regions are located in the southwestern part of Anatolia, particularly in the Vilayets of Burdur and Isparta, center of production being the village of Atabey, most of whose 3,000 inhabitants participate in the cultivation of the flowers.[104] Other, but less important, rose producing regions include Biledjik, Antalya, Konia, Brussa, Aidin, Kütahia, Afion, Karahissar.[105] In 1933 about 450 hectares were under rose in these sections of Anatolia. According to a report from Ankara,[106] the yearly production of rose flowers in the region of Isparta averages 250 metric tons in Isparta, 250 tons in Atabey and Barla, and 175 tons in Keçibarlu. Individual rose plantings are small; in 1937 there were about 1,100 rose field proprietors in Isparta and Burdur alone.[107]

The roses cultivated in Anatolia are chiefly the pink rose (*Rosa damascena* Mill.), and—to a much smaller extent—the white rose (*Rosa alba* L.), and the so-called "Hafis," a small dark red, thornless rose. The latter is cultivated mostly in Brussa; it gives a high yield of oil which, however, is inferior in quality to that of *Rosa damascena*. Rose oil dealers often use the oil from the "Hafis" for admixture with the high-grade oil from *Rosa damascena*.

The soil in which roses thrive best in Anatolia is clayey, rich in humus, slightly sandy and contains traces of ferrous salts. It should be slightly moist, not too dry. Most suitable are the slopes of hills, at 2,500 to 3,250 ft. altitude, well protected against cold north winds and hot south winds. In periods of drought the rose fields must be irrigated. The climate should be humid rather than dry; in years with ample rains the roses yield more oil than in dry years.

[104] Erhardt, *Seifensieder-Ztg.* **65** (1938), 573, 594.
[105] *Ber. Schimmel & Co.* (1933), 50. Cf. Hackforth-Jones, *Am. Perf.* **58** (1951), 257.
[106] *Öle, Fette, Wachse, Seife, Kosmetik* (1936), No. 11, p. 13.
[107] *Perfumery Essential Oil Record* **28** (1937), 384.

Digitized by Google
Original from CORNELL UNIVERSITY

New fields are started in the fall. The ground is plowed to a depth of 50 to 60 cm.; ditches, 35 to 40 cm. deep, 60 to 70 cm. wide, and 1.5 m. apart, are dug and well fertilized. In the spring the cuttings are placed into the ditches at the rate of 13,000 to 15,000 cuttings per hectare. The first worthwhile harvest can be obtained in the third year after planting, a normal harvest in the fifth year. The bushes remain productive for about twenty or twenty-five years at the most. The harvest takes place from May to June.

Distillation of the roses is carried out in numerous small open-fire stills resembling those used in Bulgaria. Some stills are fairly large—up to 1,000 liters capacity. For distillation of the oil, the flowers are boiled in ten times their weight of water. The yield of oil averages about 1 kg. per 3,000 kg. of roses.

Until 1934 Turkey's rose oil industry was a primitive house-and-village activity, entirely in the hands of numerous small producers. In that year, however, the Turkish Government, through the agency of the Sumer Bank, erected a large modern distillery in Isparta, in order to produce a rose oil of high quality which could compete with the Bulgarian product. The stills in this plant are heated with steam; 30 metric tons of roses can be processed daily. In 1938 the distillery produced about 20 per cent of Turkey's total output of rose oil.

As regards the quality of the Turkish rose oil in general, unfortunately it has not enjoyed too good a reputation on the world market. Even today it is considered inferior to the Bulgarian product. The causes are not quite clear, but several factors are probably responsible:

(a) The primitive equipment used by the peasant producers.

(b) Lack of "know-how," and faulty methods of distillation.

(c) Poor condition of the flower material (stale, slightly fermented roses, instead of fresh ones).

(d) Admixture of roses other than *Rosa damascena* Mill.

(e) Wide-spread adulteration of the oil by unscrupulous dealers and exporters. Oil of palmarosa, the so-called "Turkish Geranium Oil" for a long time has been a favored adulterant of Turkish rose oil.

That Anatolia could produce a rose oil of normal quality was demonstrated some years ago when the Turkish Government submitted samples of genuine rose oil to the Pharmazeutisches Institut of the University of Berlin for analysis.[108] The oils were found to be normal in physicochemical properties, and in odor.

Most commercial shipments, however, exhibit somewhat abnormal properties and an odor decidedly inferior to that of the Bulgarian oils. According

[108] *Ber. Schimmel & Co.* (1933), 51.

Digitized by Google Original from CORNELL UNIVERSITY

to Gildemeister and Hoffmann,[109] a sample of Anatolian rose oil, distilled from red and white roses of the Bulgarian type, had the following properties:

Specific Gravity at 30°	0.8589
Optical Rotation	−2° 20′
Refractive Index at 25°	1.46486
Congealing Point	+19.5°
Acid Number	1.4
Ester Number	9.8
Total Geraniol Content	74%

In view of the political events and the economic developments that have taken place in Bulgaria since the end of World War II, it appears highly desirable that the Anatolian rose oil industry be developed under the guidance of experts and, more important still, that the Government of Turkey take energetic steps to stop the wide-spread practice of adulteration, from which in the past the Anatolian oil has suffered most.

III. The French Rose Oil Industry

The rose oil industry of the Grasse region in Southern France differs from the Bulgarian chiefly in two respects:

(a) The rose grown in the Grasse region for industrial purposes is *Rosa centifolia* L., locally called "Rose de Mai," a light pink-colored rose related to the Bulgarian (and Turkish) *Rosa damascena* Mill.

(b) On hydrodistillation, *Rosa centifolia* gives a smaller yield of oil than *Rosa damascena;* hence in the Grasse region the roses are extracted with volatile solvents, yielding the concrete and absolute of rose (cf. Vol. I of the present work, pp. 200 ff.). Before the introduction of this modern process, the flowers were treated by maceration with hot fat (cf. Vol. I, p. 198), which gave the so-called *"Pommades"* and *"Extraits de Rose."* A small quantity of the roses in the Grasse region has always been processed by distillation—not to isolate the volatile oil, but to prepare the fragrant rose water so popular in Mediterranean and Latin countries for flavoring, cosmetic, and pharmaceutical purposes.

Producing Regions, Planting, and Cultivation.—The rose plantations—all relatively small and mostly operated by individual farmers and their families—are located near Grasse, Pégomas, Mougin, Montauroux, and other parts of that picturesque and beautiful country; two-thirds of the crop comes from La Colle, Grasse, and Saint-Paul de Vence. In 1939 the extraction plants of the Grasse region processed altogether 750,000 kg. of roses; in 1946 the quantity declined to about 400,000 kg. (Girard [110]). In 1949 the

[109] "Die Ätherischen Öle." 3d Ed., Vol. II, 822.
[110] *Ind. parfum.* **2** (1947), 185.

Digitized by Google
Original from CORNELL UNIVERSITY

Grasse region produced 500,000 kg. of roses, in 1950 only 300,000 kg.[111] According to Ellmer,[112] roses cultivated in the higher altitudes (about 1,150 m.) yield from 30 to 35 per cent more concrete than the flowers from the plains (100 to 250 m. altitude).

In the Grasse region the roses are usually grown on nonirrigated land for the simple reason that they withstand spells of drought better than other flowers—jasmine, e.g. As a rule, however, rose bushes require water. Plantings are started in the fall, after deep plowing of the soil. According to Arnaud,[113] *Rosa centifolia* is propagated not by grafting, but by means of carefully selected, vigorous, and healthy suckers, planted 0.7 by 1.5 m. apart. To keep the ground in good condition, it should be frequently plowed, and dressed with organic and inorganic fertilizers. To obtain a high yield of flowers per branch, the latter should be allowed to grow as long as possible and trained into a horizontal position. This can be effected by preserving, in the pruning operation, two or three long stems which are intertwined with the branches of the neighboring rose bush. In this operation old woody stems that have already produced their share of flowers are cut out, and the young shoots are properly dressed for new flower growth.

Harvesting starts in the second year after planting, reaching its maximum in the fifth year. After twelve years the productivity of a planting declines rapidly. On the average, a single rose bush produces 250 g. of flowers per season. A yield of 3,000 kg. of roses per hectare is considered very satisfactory. The harvest takes place in May, very early every morning (from 4 to 8 A.M.), before the dew has disappeared from the flowers. One harvester can pick from 4 to 10 kg. of roses per hour. After collection, the roses should be processed as soon as possible; otherwise they will wither and give a poor yield on extraction.

A. Distilled Rose Oil

Years ago relatively large quantities of "Rose de Mai" were processed in the Grasse region by hydrodistillation for the production of fragrant rose water. To a limited extent this is still practiced. For this purpose 1,000 kg. of *Rosa centifolia* L. are charged into a still and boiled in water until 1,000 liters of water have distilled over. This water is not redistilled (cohobated) and represents the commercial "Rose Water." In the process of distillation about 100 g. of (direct) rose oil separate in the Florentine flask. This quantity corresponds to a yield of 1 kg. of rose oil per 10,000 kg. of *Rosa centifolia* L., as compared with 1 kg. of rose oil per 4,000 kg. of *Rosa damascena*

[111] *Soap, Perfumery & Cosmetics* **23** (1950), 913.
[112] *Riechstoff Ind.* **5** (1930), 193.
[113] *Ind. parfum.* **4** (1949), 367.

Digitized by Google Original from CORNELL UNIVERSITY

Mill., obtained in Bulgaria. (It must, however, be kept in mind that in Bulgaria the rose water is repeatedly cohobated in order to recover the relatively large quantity of rose oil suspended and dissolved therein. The yields indicated above, therefore, do not represent the actual oil contents of the two rose species.) The rose oil thus obtained in the Grasse region is only a by-product in the preparation of rose water; it is usually not sold on the market as a commercial product, but used by the essential oil houses of Grasse (mostly in perfume compositions).

A French rose oil obtained in the manner described above (without cohobation of the distillation water) was examined by Jeancard and Satie [114] who reported these properties:

Congealing Point	+25.9°
Acid Number	2.24
Saponification Number	14.70
Total Alcohol Content	32%
Citronellol Content	15.10%
Stearoptene Content	58.88%

As regards the rose water—it must meet the standards of the various Pharmacopoeias. To protect it from infestation by microorganisms, it should be stored in very clean containers, in a dark and cool place.

B. Extracted Rose Oil
(Concrete and Absolute of Rose)

As was said above, by far the greater part of the roses (*Rosa centifolia* L., or "Rose de Mai") grown in the Grasse region of Southern France are now worked up by the modern process of extraction with volatile solvents, thereby yielding concrete and absolute of rose. The solvent most generally used is petroleum ether which, according to Naves and Mazuyer,[115] yields from 0.24 to 0.265 per cent of concrete, the wider limits being 0.17 to 0.27 per cent. The concrete gives from 55 to 65 per cent of alcohol-soluble absolute, and contains from 25 to 32 per cent of steam-volatile oil. In the experience of the author of the present work, from 400 to 500 kg. of *Rosa centifolia* L. are required to produce 1 kg. of concrete; the latter yields from 500 to 600 g. of absolute.

There is another type of rose cultivated on the French and Italian Riviera, principally for use as an ornamental flower. This is the so-called "Rose Brunner"; flowers that cannot be sold to florists are occasionally purchased by the extraction plants in Grasse and processed with volatile solvents.

[114] *Bull. soc. chim.* [3], **31** (1904), 934.
[115] "Les Parfums Naturels," Paris (1939), 268.

Digitized by Google Original from CORNELL UNIVERSITY

According to Naves and Mazuyer,[116] the yield of concrete from "Rose Brunner" ranges from 0.10 to 0.14, occasionally to 0.19 per cent; the concrete gives from 30 to 35 per cent of absolute. Because of the poor yield and odor, only insignificant quantities of concrete and absolute are produced from "Rose Brunner."

Physicochemical Properties.—Concrete of rose extracted from *Rosa centifolia* L. ("Rose de Mai") with petroleum ether (the usual solvent) is a waxy, light to dark brown mass with a characteristic and strong rose odor. Compared with that of the Bulgarian concrete (from *Rosa damascena* Mill.), the odor of the French product is softer and more spicy, less reminiscent of distilled rose oil.

Girard [117] (I), and Naves and Mazuyer [118] (II) reported these properties for rose concrete from "Rose de Mai":

	I	*II*
Congealing Point	+52° to +53°	+43° to +48°
Melting Point	...	+49° to +54°
Optical Rotation	+10° 20′	...
Refractive Index at 60°	1.4811	...
Acid Number	14.28	9.8 to 14.4
Ester Number	23.1	19.6 to 25.2

The corresponding *absolute* is a yellowish to light brown viscous liquid with a strong and very lasting rose odor.

The following properties are those noted by Schimmel & Co.[119] for a French absolute of rose (I), by Naves [120] for three absolutes from the Département of Var in Southern France (II), and by Girard [121] for absolutes from Grasse (III). All oils were extracted from "Rose de Mai":

	I	*II*	*III*
Specific Gravity at 15°	0.9640	0.981 to 0.993	0.964 to 0.988
Optical Rotation	+13° 55′	+10° 41′ to +13° 10′	+10° 41′ to +13° 55′
Refractive Index at 20°	1.50873	1.5096 to 1.5122	1.5087 to 1.5104
Acid Number	9.3	3.4 to 7.56	3.4 to 9.3
Ester Number	29.0	17.5 to 26.6	17.5 to 29
Ester Number after Acetylation	220.3	229.9 to 236.6	...

As was pointed out above, the concrete and absolute of rose contain volatile oils which are occasionally isolated in the laboratory, by steam distilla-

[116] *Ibid.*, 269.
[117] *Ind. parfum.* **2** (1947), 185.
[118] "Les Parfums Naturels," Paris (1939), 269.
[119] *Ber. Schimmel & Co.* (1926), 104.
[120] "Les Parfums Naturels," Paris (1939), 269.
[121] *Ind. parfum.* **2** (1947), 185.

Digitized by Google Original from CORNELL UNIVERSITY

tion at reduced pressure, in order to check the purity of the corresponding concrete or absolute. These volatile oils are not commercial products, however. Naves, Sabetay and Palfray [122] examined a volatile oil which they had obtained from an extraction product of "Rose de Mai":

Specific Gravity at 15°	0.976
Optical Rotation	−2° 24′
Refractive Index at 20°	1.5038
Acid Number	0.8
Ester Number	7.2
Ester Number after Acetylation	292.6

Chemical Composition.—The chemical composition of the volatile constituents present in the concrete and absolute of *Rosa centifolia* L. was investigated by von Soden,[123] and Elze [124] who identified the following compounds:

Phenylethyl Alcohol. The principal constituent. Treating the volatile oil (derived from French rose extracts) with phthalic anhydride, von Soden isolated 75 to 80 per cent of alcohols; these consisted of 75 per cent of phenylethyl alcohol and 25 per cent of other primary alcohols—the latter identical with those occurring in distilled rose oil.

Geraniol. Reported by Elze. Diphenylurethane m. 81°–81.5°.

Citronellol. Characterized by oxidation to citronellal, which was identified by means of the naphthocinchoninic acid compound m. 225° (Elze).

Nerol. Preparation of the diphenylurethane m. 50°–50.5° (Elze).

Farnesol. Reported by Elze.

According to Naves,[125] concrete of rose also contains small quantities of *eugenol, eugenol acetate,* and traces of a ketone with a minty odor. However, Naves does not specify whether the rose concrete from which he isolated these compounds was of French or Bulgarian origin.

IV. The Moroccan Rose Oil Industry

Most probably the rose plant was introduced to Morocco by the Moslem Arabs in the seventh century A.D., when they swept over the whole of North Africa and founded the Ommiad Caliphate. Since then the rose has remained the favorite flower of the Moors, who grow it in cities and villages for ornamental purposes and for distillation of rose water. Next to gera-

[122] *Perfumery Essential Oil Record* **28** (1937), 336.
[123] *J. prakt. Chem.* [2], **69** (1904), 265.
[124] *Chem. Ztg.* **43** (1919), 747.
[125] Naves and Mazuyer, "Les Parfums Naturels," Paris (1939), 271.

Digitized by Google
Original from CORNELL UNIVERSITY

nium, the rose is today perhaps the most widely cultivated of all North African perfume plants. For centuries the production of rose water has been a picturesque home industry practiced by the families of wealthier natives, particularly in Morocco. The perfumed water thus prepared serves for toilet requirements and for the flavoring of beverages and confectionery. In the primitive process the essential oil is seldom collected because the distillation water would have to be cohobated to obtain an appreciable yield of oil.

The rose cultivated in Morocco was formerly thought to be *Rosa damascena* Mill. In 1930, however, the botanist Jean Gattefossé made an expedition to various oases in the southern part of Morocco, where roses grow abundantly at altitudes ranging from 3,000 to 4,800 ft.; he identified the plant as belonging to the species cultivated in Southern France, viz., *Rosa centifolia* L.[126] The observations of Gattefossé have shown that in Morocco the rose bushes thrive at much higher altitudes than in the Grasse region of Southern France; they are capable of resisting very wide ranges of temperature and particularly drought—provided the soil is properly taken care of. As a matter of fact, "rust," that dreaded disease which frequently attacks rose bushes growing in humid or irrigated soil, is almost unknown in certain parts of southern Morocco.

While the rose bush of Marrakesh, the most popular of all Moroccan roses, is of the species *Rosa centifolia* L., there seem to be other types in southern Morocco—e.g., in Mesguita, south of Quarzazat—which belong to the species *Rosa damascena* Mill. It is quite possible that the original rose stock, introduced by the Arabs (perhaps from Persia) was *Rosa damascena,* or even a more primitive parent species, but that as a result of ecological and cultural factors the plant underwent morphological changes and finally developed into *Rosa centifolia* and closely related species. It is a well-known fact that species of *Rosa* hybridize very easily.

The rose producing regions of Morocco are located chiefly between the High Atlas in the north and the Djebel Sarro in the south. Here the bushes are grown not on special plantations, but in rows between trees, and in the form of dense hedges surrounding gardens, wheat, and leguminous fields. The bushes may attain a height of 6 ft., and each bush produces thousands of blossoms. The roses are clipped off in March and April before the buds have opened and are then dried in the sun—a simple process in the warm and dry climate of Morocco. Five kilograms of fresh buds yield about 1 kg. of dried buds. According to Igolen,[127] native producers and dealers distinguish several qualities, the lowest being the so-called "Entifa" and "Glaoua," the next "Skoura," and the best "Daddès." Center of the trade

[126] Trabaud, *Drug Cosmetic Ind.* **40** (1937), 782.
[127] *Rev. marques parfums France* **17** (1939), 175.

Digitized by Google Original from CORNELL UNIVERSITY

in dried roses is the old and picturesque city of Marrakesh; here large quantities of dried rose buds arrive by caravan from distant oases in the south and southwest. Before World War II Morocco produced from 400 to 750 metric tons of dried rose buds per year; one-third of this quantity was exported to Marseilles and New York, two-thirds was used locally for the preparation of rose water by small-scale native distillers.

Hydrodistilling dried Moroccan rose buds, Igolen [128] obtained 0.03 per cent of a rose oil, which at room temperature was a greenish, solid mass with these properties:

Congealing Point	+27°
Melting Point	+28.7°
Specific Gravity at 15°	0.8628
Optical Rotation at 25°	±0°
Refractive Index at 25°	1.4627
Acid Number	19.6
Ester Number	35.07
Ester Number after Formylation	68.74
Rhodinol Content	19.8%

The oil exhibited the characteristic, slightly unpleasant, hay-like odor of the dried buds.

Extracting dried Moroccan rose buds with petroleum ether, the same author [129] obtained a dark green, semisolid concrete (melting point 46°–47°, acid number 18.2, ester number 64.4) which on steam distillation and cohobation of the distillation waters yielded 1.05 per cent of a volatile oil with the following properties:

Congealing Point	+11°
Specific Gravity at 15°	0.8666
Optical Rotation	−0° 20′
Refractive Index at 20°	1.4637
Acid Number	16.8
Ester Number	39.2
Ester Number after Acetylation	129.06
Ester Number after Formylation	105.2
Rhodinol Content	30.9%

Investigating this oil more closely, Igolen found that it contained relatively large quantities of *phenols*, *aldehydes* (*benzaldehyde* and perhaps *nonylaldehyde*) and free *acids*. The benzaldehyde probably originated during the drying process of the rose buds, by oxidation of certain degradation products.

In the course of the past thirty years several attempts have been made by French concerns to improve the rose industry in Morocco and to produce

[128] *Ibid.* [129] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

distilled rose oil as well as concretes in modern equipment. For example, at Sebaa-Aioun [130] a factory has been equipped not only for the distillation of roses, but also for extraction by the volatile solvent process. Because dried rose buds are used, the products obtained in this plant differ from those of the Grasse region, but certain perfumers have been using them for some time with quite satisfactory results.

According to Trabaud,[131] another attempt along similar lines was made near Meknès, at 1,600 ft. altitude, where many acres of a thornless variety of *Rosa centifolia* L. were planted under ideal conditions by the same French concern. This variety is a hybrid produced from a crossing of *Rosa centifolia* and *Rosa indica*. It produces more flowers, but their perfume is not quite so fine as that of the thorny variety. Yield of distilled oil approximates that obtained in Bulgaria, viz., 1 kg. of oil per 3,000 to 4,000 kg. of flowers. The oil has a yellow, slightly greenish color, and a delicate odor differing quite markedly from that of the Bulgarian distilled oil (*Rosa damascena*). Its aroma resembles that of the *Rosa centifolia* grown in the Grasse region of Southern France. For oils distilled in 1933, 1935, and 1936 Trabaud reported these properties:

Complete Oil	*1933*	*1935*	*1936*
Stearoptene Content	13%	15%	17.5%
Congealing Point	+22°	+20°	+20.5°
Melting Point	+23.5°	+20.5°	+21°
Specific Gravity at 15°	0.873	0.871	0.8706
"Elaeoptene" (Liquid Portion)			
Congealing Point	−9°	−10°	−15°
Specific Gravity at 15°	0.8782	0.885	0.8805
Optical Rotation	−2° 0′	−2° 0′	−2° 10′
Refractive Index at 20°	...	1.4702	1.4523
Acid Number	2.5	0.8	0.9
Ester Number	13.75	14	7.4
Ester Number after Acetylation	263.2	253.87	261.3
Total Alcohol Content	90%	86.23%	89.4%
Geraniol Content	37%	50%	55.5%
Citronellol Content (By Formylation)	50%	32%	31.8%

Compared with that of the Bulgarian oils, the stearoptene content of the Moroccan oils is very low; the percentage of total alcohols approximates the upper limits found in Bulgarian oils.

Because of its small production, the Moroccan distilled rose oil is not yet well known in the trade. According to Trabaud,[132] however, the oil may well serve as a replacement for the very expensive (distilled) "Rose de Mai"

[130] Trabaud, *Drug Cosmetic Ind.* **40** (1937), 816.
[131] *Ibid.* [132] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

oil from Grasse, production of which has been practically abandoned in favor of the (extracted) concrete.

An entirely new chapter in the rose industry of Morocco was opened when in 1941 an experienced and progressive essential oil producer from Southern France started large-scale plantations of aromatic plants near Khemisset, about halfway between Rabat and Meknès. Details of this development are given in the monographs on "Oil of Geranium Moroccan" [Vol. IV of the present work, p. 709, and "Concrete and Absolute of Jasmine" (Morocco)—this volume, p. 323]. After selection of the most suitable locality, plantations were started with modern farming equipment; and carefully selected, vigorous stocks of *Rosa centifolia* L. imported from the Grasse region of Southern France were planted. Great difficulties were encountered at first; indeed, it was only in 1950 that the plantations began to produce.[133] Planting was done as with grape vines in Algeria, and with similar spacing between plants—i.e., 1.5 m. between rows and 1 m. between individual plants in the same row. This method permitted setting out only 4,000 cuttings per hectare. In the pruning operation, the time-honored method practiced in the Grasse region was followed: the rose shoots were trained to grow horizontally (by intertwining branches of adjacent bushes). In this position, they bear more flowers. Use of special cultural techniques along the principles of dry farming (frequent tillage, dressing, etc.) obviated irrigation of the rose fields, which may cause the worst of all rose diseases—rust. In spite of the fact that the number of plants per hectare is much smaller than is usual in Southern France, the yield of roses per hectare in Morocco approaches that of the Grasse region (2 to 3 metric tons). However, yield of concrete from the flowers is smaller than that obtained in France, 1,000 kg. of roses yielding less than 2 kg. of concrete. In France the rose harvest lasts only about two weeks; in Morocco flowers can be gathered for almost two months. The picking is done by hundreds of native children, in the very early morning hours, starting at dawn. The freshly harvested roses are brought to the modern extraction plant located in the center of the flower fields, and extracted with petroleum ether immediately upon arrival. Concretes and absolutes of rose produced in Khemisset have been favorably received by perfumers. Provided no unforeseen events interfere with this new development, it may well become a serious competitor of the Grasse industry.

V. The Russian Rose Oil Industry

Comparatively little is known about the production of rose oil in the U.S.S.R.

[133] Private communication from Mr. Pierre Chauvet, Seillans (Var), France.

Digitized by Google Original from CORNELL UNIVERSITY

(*Top*) Rose distillation in Bulgaria. A battery of old-fashioned direct fire stills. (*Left*) A modern rose distillery in Bulgaria equipped with direct fire stills. (*Right*) Separation of the condensate into rose oil and distillation water. *Photos Fritzsche Brothers, Inc., New York.*

Digitized by Google
Origi
CORNELL

(*Top*) East Indian nutmeg. The whole nutmeg fruit, and cut fruit showing the mace surrounding the shell which encloses the nutmeg. (*Bottom*) Nutmeg production in Grenada, B. W. I. Sun-drying of nutmegs on large wooden trays (barbecues). The nutmegs have to be turned over from time to time. *Photos Fritzsche Brothers, Inc., New York.*

Digitized by Google
Original from CORNELL UNIVERSITY

In 1937 Kitchounow [134] reported that roses of the Kazanlik type (one variety with pink flowers and another variety with red flowers) had been planted in the Crimean Peninsula, the total acreage covering 350 hectares, and one hectare comprising 4,000 rose bushes. The yield of flowers can be substantially increased by irrigation from May to August. The harvest takes place from the end of May to the beginning of June. If the flowers are picked after 10 A.M., the yield of oil is as much as 59 per cent lower than when they are collected in the early morning. If possible, the plants are propagated by means of suckers, which give better results than young plants.

According to Schimmel & Co.[135] the first experiments in growing roses in the Crimea were undertaken by the Soviet Government about 1930, in the Nikita Gardens near Yalta. The first plantings in the field were laid out on the southern slopes of the Jaila Mountains and later were extended into the plains to the north of these mountains. Distillation of the flowers was carried out in several distilleries. The plantations suffered during World War II, but some rose oil was produced under the direction of German experts.

According to another trade report,[136] the so-called "Valley of the Roses" ("Dolina Ros") on the Crimean Peninsula in 1941 contained about 70 hectares of Kazanlik roses. The flowers were distilled by the same government corporation that owned the fields. The districts of Lagodechski and Telavski in the Georgian Soviet Republic also started cultivation of roses on a rapidly increasing scale. To what extent these developments were affected by World War II is difficult to ascertain. Quite possibly the Soviet Government is now attempting to produce rose oil on a larger scale than before the war.

Use of Oil, Concrete, and Absolute of Rose

Oil of rose is one of the oldest and most valuable perfumers' materials. It would not be an exaggeration to say that no high-grade perfume is complete that does not contain at least small quantities of rose oil, which lends beauty and depth to odor blends.

The distilled oil of rose imparts characteristic flowery top notes to perfumes; the extracted absolute adds lasting tonalities and increases fixation of odors. A mixture of distilled oil and extracted absolute combines the advantages of the two products.

Where solubility in dilute alcohol is important, the distilled oil will have to be employed; the absolute is soluble only in high-proof alcohol and can

[134] *Parfumerie moderne* **31** (1937), 175.
[135] *Ber. Schimmel & Co.* (1942/43), 59.
[136] *Chem. Ind.* **64** (1941), 366.

Digitized by Google Original from CORNELL UNIVERSITY

therefore be used only in handkerchief perfumes, or in cosmetics where solubility plays no role. In powders and creams even the much lower priced concretes (which are only partly soluble in high-proof alcohol) may give excellent results.

For many years, large quantities of distilled rose oil have been used for the flavoring of certain types of tobacco, particularly snuff and chewing tobacco. Limited quantities of the oil are employed also in the flavoring of soft drinks and alcoholic liqueurs.

Suggested Additional Literature

G. Maranca, "Le Parfum des Feuilles de Rosier de Mai," *Ind. parfum.* **3** (1948), 360.

Paul Langlais et Jean-Louis Bollinger, "Recherches dans le Domaine des Parfums Naturels. L'Hydrolyse des Glucosides de la Rose," *Ind. parfum.* **2** (1947), 13.

A. Janistyn, "Rosen von Dadès," *Parfümerie Kosmetik* **32** (1951), 248.

OIL OF BITTER ALMOND

Essence d'Amandes Amères *Bittermandelöl*
Aceite Esencial Almendras Amargas *Oleum Amygdalarum Amararum*

Bitter almond oil is the volatile oil derived, by steam distillation, from the dried, ripe kernels of *Prunus amygdalus* Batsch var. *amara* (DC.) Focke (fam. *Rosaceae*), or from other kernels containing amygdalin. Prior to distillation, the kernels must be freed of their fatty (fixed) oil by expression, and the powdered pressed cake must be macerated in warm water in order to split the glucoside amygdalin (see below).

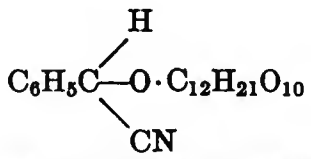
The bitter almond tree is widely cultivated in Southern Europe (particularly Spain), North Africa (Morocco and Algeria), Asia Minor, and lately also in California. However, in modern industrial production of bitter almond oil the kernels of the bitter almond tree have for quite some time been replaced by lower priced and higher yielding kernels of other fruit trees, *which contain amygdalin* and yield an essential oil that cannot be distinguished from that of the bitter almonds. Obviously only bitter kernels can be used in the production of the volatile oil. Most important among them are apricot kernels (commercially often called "peach kernels"), large quantities of which have been imported to Europe and the United

Digitized by Google Original from CORNELL UNIVERSITY

States from Morocco, Syria, Asia Minor, and the Far East (China and Japan).

A new supply has been opened in the last twenty years with the availability of substantial quantities of stones and kernels obtained as by-products in fruit canning. Tilgner[1] reported that the stones of apricots yield from 22 to 25 per cent of kernels, those of peaches 7 per cent, cherries 28 per cent, and plums 12 per cent of kernels. The kernels are heated to 85° C. and pressed, first in a continuous conical press and then in a hydraulic press at a pressure of at least 350 kg. per sq.cm. Apricots thus give 35 per cent of fatty (fixed) oil, peaches 25 per cent, cherries and plums 30 per cent. After filtration the fatty oil is neutralized with sodium carbonate and decolorized with Fuller's earth or charcoal. According to Gildemeister and Hoffmann,[2] bitter almonds, on *cold* expression, yield about 50 per cent, apricot kernels from 35 to 38 per cent, of fatty oil.

The essential (volatile) oil is not present as such in the kernels, but in the form of a cyanogenetic glucoside, viz., amygdalin, which has this constitution:



(Mandelonitrile-gentiobioside)

Under the influence of the enzyme emulsin, the amygdalin is decomposed into a molecule of benzaldehyde, a molecule of hydrocyanic acid, and two molecules of glucose, according to the following reaction:

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water}}{2H_2O} \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\substack{\text{Hydro-}\\\text{cyanic}\\\text{Acid}}}{HCN} + \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Distillation.—For commercial production of the essential oil the pressed cake is powdered, mixed with ten parts of water, and permitted to macerate for about 12 hr. at a temperature ranging from 50° to 60° C. During this period the emulsin, which is present in the kernels and freed by crushing of the latter, reacts upon the amygdalin. To induce and accelerate the process it may be advisable to add to the mass a small quantity of warm water thoroughly mixed with finely powdered bitter almond kernels. After complete hydrolysis of the amygdalin by means of emulsin, the mass is steam distilled. Because of the toxicity of the hydrocyanic acid originating

[1] *Konserven Ind.* **18** (1931), 257. *Chem. Abstracts* **25** (1931), 4322.
[2] "Die Ätherischen Öle," 3d Ed., Vol. II, 844.

Digitized by Google Original from CORNELL UNIVERSITY

during the process, utmost caution must be exercised in the course of distillation. Since poisonous hydrocyanic acid vapors may escape into the room, the oil separator and receiver should be tightly enclosed. Any vapors that cannot be condensed should be conducted into the open air where they can do no harm. Moreover, the distillation waters, in which substantial quantities of hydrocyanic acid are dissolved, should also be properly disposed of. In some countries, the distillation waters discarded from a rural distillery serve for irrigation or for watering of cattle; in the case of bitter almond distillation this must be strictly avoided.

The residual powdered material can be pressed into cakes and used as cattle feed.

Yield of Oil.—Benzaldehyde, the chief constituent of bitter almond oil, is quite soluble in water. In order to obtain the bulk of the oil, the distillation water must therefore be redistilled (cohobated).

Gildemeister and Hoffmann [3] reported that bitter almonds yield from 0.5 to 0.7 per cent, apricot kernels from 0.6 to 1.8 per cent of volatile oil. According to Tilgner [4] peach kernels give about 0.7 per cent, apricot kernels 1.2 per cent, plum kernels 0.4 per cent, and cherry kernels 0.6 per cent of volatile oil. Apricot kernels, therefore, represent the best starting material for the production of bitter almond oil.

Oil of bitter almond contains from 2 to 4 per cent of hydrocyanic acid. To remove the latter, if so required, the oil is shaken with milk of lime and iron vitriol (hydrous ferrous sulfate), whereby the hydrocyanic acid is precipitated as insoluble calcium ferrocyanide. The remaining benzaldehyde is then steam distilled. Provided the operation has been properly conducted the rectified oil contains no trace of hydrocyanic acid. (Re Prussian Blue Test, see Vol. I of this work, p. 304.) Tilgner [5] recommended adding sodium sulfite to the oil and distilling the mass, in order to remove the hydrocyanic acid.

Physicochemical Properties.

(*a*) *Oil Containing Hydrocyanic Acid.*—Oil of bitter almond, which contains hydrocyanic acid, is a colorless, highly refractive liquid, exhibiting the typical odor of chewed bitter almonds. On aging of the oil its color turns yellow. Because of its toxicity the oil should be smelled with great caution.

Gildemeister and Hoffmann [6] reported these properties for bitter almond oil from which the hydrocyanic acid has *not* been removed:

[3] *Ibid.*, 847.
[4] *Konserven Ind.* **18** (1931), 257. *Chem. Abstracts* **25** (1931), 4322.
[5] *Ibid.*
[6] "Die Ätherischen Öle," 3d Ed., Vol. II, 847.

Digitized by Google
Original from CORNELL UNIVERSITY

Specific Gravity at 15°	1.045 to 1.070 (a higher specific gravity indicates an abnormally high content of hydrocyanic acid or, more correctly, of benzaldehyde cyanohydrin. For further details see the section on "Chemical Composition," below)
Optical Rotation	In most cases optically inactive; in a few instances very slightly dextrorotatory, up to +0° 9′
Refractive Index at 20°	1.532 to 1.544 (the magnitude of the refractive index is inversely proportional to the hydrocyanic acid content)
Hydrocyanic Acid Content	Varies greatly and is much higher in crude oils than in rectified oils. In a crude oil (d_{15} 1.090, n_D^{20} 1.52986) as much as 11% of hydrocyanic acid was observed; in a rectified oil (d_{15} 1.053, n_D^{20} 1.54497) only 0.56% was found (see also below)
Benzaldehyde Content	Must conform to the requirements of the various pharmacopoeias (see also below)
Solubility	The oil is quite soluble in water, 1 vol. of oil being soluble in about 300 vol. of *pure* water. Water containing hydrocyanic acid dissolves the oil even more readily. The oil is soluble in 1 to 2 vol. and more of 70% alcohol; soluble in 2.5 vol. and more of 60% alcohol; on aging, the oil loses its solubility in 60% alcohol

Pure oils of bitter almond (containing hydrocyanic acid) examined by Fritzsche Brothers, Inc., New York, had properties varying within the following limits:

Specific Gravity at 25°/25°	1.049 to 1.058
Optical Rotation	Inactive to +0° 11′
Refractive Index at 20°	1.5403 to 1.5435
Aldehyde Content, Calculated as Benzaldehyde (Hydroxylamine Hydrochloride Method)	81.3 to 93.2%
Total Hydrocyanic Acid Content (Including Benzaldehyde Cyanohydrin)	2.1 to 4.0%
Halogen Test	Negative
Heavy Metals Test	Negative
Solubility	Soluble in 1 to 2 vol. of 70% alcohol; sometimes slightly hazy upon further dilution. Usually soluble in 5 to 6 vol. of 50% alcohol; sometimes with slight opalescence or haze
Solubility in Bisulfite Solution	Slight oily separation

As regards the content of benzaldehyde, it should not be less than 80 per cent. In most oils the aldehyde content, calculated as benzaldehyde, ranges

Digitized by Google Original from CORNELL UNIVERSITY

from 84 to 87 per cent. For method of determination, see Vol. I of the present work, p. 286.

Regarding the content of hydrocyanic acid, it should not be less than 2 per cent and not more than 4 per cent. For quantitative determination, see Vol. I of the present work, pp. 304, 305.

Freshly distilled bitter almond oil is neutral, but on aging the oil becomes acidic, because of oxidation of benzaldehyde to benzoic acid.

When oil of bitter almond is distilled over direct fire (caution: development of hydrogen cyanide vapors) the first fractions will contain substantial quantities of hydrogen cyanide, the later fractions much less. The distillation residue contains benzoin, a product originating by polymerization of two molecules of benzaldehyde under the influence of hydrocyanic acid:

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Benzaldehyde}}{OHCC_6H_5} \xrightarrow[HCN]{} \underset{\text{Benzoin}}{C_6H_5CH(OH)COC_6H_5}$$

(*b*) *Oil Free of Hydrocyanic Acid.*—Oil of bitter almond from which the hydrogen cyanide has been removed consists almost entirely of benzaldehyde and may justly be called natural benzaldehyde.

According to Gildemeister and Hoffmann [1] the oil has these properties:

Boiling Point	179°
Specific Gravity at 15°	1.050 to 1.055 (a higher specific gravity may be caused by a greater content of benzoic acid)
Optical Rotation	Optically inactive
Refractive Index at 20°	1.542 to 1.546
Solubility	Soluble in 1 to 2 vol. and more of 70% alcohol

This type of oil is much more sensitive to oxidation by air than the oil which contains hydrogen cyanide. The latter acts as a preservative. Pure benzaldehyde is readily oxidized to benzoic acid by exposure to air.

Adulteration.—At one time bitter almond oil was occasionally adulterated with nitrobenzene; but this crude form of adulteration is no longer encountered.

A much more annoying adulterant is synthetic benzaldehyde because it cannot be detected readily. In past years the synthetic benzaldehyde used for this purpose sometimes contained chlorine, the result of improper purification. Such benzaldehyde could then be detected quite readily by the Halogen Test, details of which will be found in Vol. I of this work, pp. 307,

[1] *Ibid.*, 848.

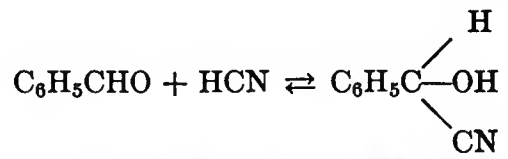
Digitized by Google Original from CORNELL UNIVERSITY

308. Today, however, the Halogen Test has lost much of its importance because synthetic benzaldehyde is now produced in a high state of purity.

Storage.—Oil of bitter almond has to be stored in well-filled and well-stoppered bottles in order to prevent any access of air. Otherwise, part of the benzaldehyde will be oxidized to benzoic acid. As was mentioned above, oils containing hydrogen cyanide are much more stable than oils from which the hydrogen cyanide has been removed.

Schimmel & Co.[8] found that alcohol added in the amount of 10 per cent acts as a preservative of the oil. On the contrary, if only 5 per cent of alcohol is added, oxidation takes place even more rapidly than in the undiluted oil. This applies to both types of oil.

Chemical Composition.—As was explained above, splitting of the cyanogenetic glucoside amygdalin under the influence of the enzyme emulsin results in the formation of benzaldehyde, hydrocyanic acid, and glucose. Distillation of the reaction products yields a volatile oil composed chiefly of benzaldehyde and a small quantity of hydrocyanic acid, the greater part of the latter being dissolved in the distillation water. On prolonged contact of benzaldehyde with hydrocyanic acid the following reaction takes place:



In other words, benzaldehyde and hydrocyanic acid combine to form benzaldehyde cyanohydrin.[9] However, the latter compound is readily decomposed into its components, even on steam distillation or on distillation *in vacuo*. Therefore, benzaldehyde cyanohydrin originates only *after* distillation of the reaction mass, particularly when the oil is left standing for some time in contact with distillation water that contains substantial quantities of hydrocyanic acid.

That bitter almond oil actually contains benzaldehyde cyanohydrin was proved more than seventy years ago by Fileti,[10] who reduced bitter almond oil and obtained phenylethylamine. Reduction of a freshly prepared mixture of benzaldehyde and hydrocyanic acid, on the other hand, yielded only methylamine.

Benzaldehyde cyanohydrin possesses a relatively high specific gravity

[8] *Ber. Schimmel & Co.*, April (1895), 47.
[9] Cf. Wirth, *Arch. Pharm.* **249** (1911), 382.
[10] *Gazz. chim. ital.* **8** (1878), 446. Cf. *Ber.* **12** (1879), 297.

Digitized by Google Original from CORNELL UNIVERSITY

(d 1.124). Therefore, the more benzaldehyde cyanohydrin a bitter almond oil contains, the higher will be its specific gravity and the greater will be its content of hydrocyanic acid. According to Gildemeister and Hoffmann [11] normal bitter almond oils with a specific gravity of 1.052 to 1.058 contain from 1.6 to 4 per cent of hydrocyanic acid, while oils with a specific gravity of 1.086 to 1.096 contain from 9 to 11.4 per cent of hydrocyanic acid. Experiments carried out by Schimmel & Co.[12] showed that the specific gravity of pure benzaldehyde increased from 1.054 to 1.074, after the aldehyde had been left in contact with a 20 per cent aqueous solution of hydrocyanic acid for two days.

Aside from benzaldehyde, hydrocyanic acid, and benzaldehyde cyanohydrin, oil of bitter almond most likely contains traces of other substances which are responsible for the finer odor and flavor of natural benzaldehyde isolated from the oil, as compared with the synthetic product. These trace substances have not yet been identified (cf. Dodge, Eighth International Congress of Applied Chemistry, Washington and New York, Vol. 17 [1912], 15).

Use.—Oil of bitter almond is a very important flavoring agent, used particularly in baked goods, cakes, confectioneries, and candies. However, for the scenting of cosmetics, soaps, and technical preparations, the much lower priced synthetic benzaldehyde is now employed almost exclusively.

OIL OF CHERRY LAUREL

Essence de Laurier Cerise *Kirschloorbeeröl*
Aceite Esencial Laurel Cerezo *Oleum Laurocerasi*

Prunus laurocerasus L. (fam. *Rosaceae*), our common cherry laurel, is an evergreen bush or small tree, native of southeastern Europe and Asia Minor. It is cultivated as an ornamental plant in many temperate countries. In Southern France, Italy, and other Mediterranean countries the leaves are distilled, whereby an aromatic water, the so-called cherry laurel water, is obtained.

The leaves contain a monoglucoside, viz., *prulaurasin* $C_{14}H_{17}O_6N$, which, according to the recent work of Rosenthaler [1] is the nitrile glucoside of

[11] "Die Ätherischen Öle," 3d Ed., Vol. II, 849.
[12] *Ber. Schimmel & Co.*, April (1893), 42.
[1] *Pharm. Acta Helv.* **19** (1944), 100.

Digitized by Google Original from CORNELL UNIVERSITY

l-mandelic acid. Splitting of the glucoside prulaurasin by means of emulsin yields 61.24 per cent of β-glucose, 8.58 per cent of hydrocyanic acid, and benzaldehyde. In the industrial production of cherry laurel water it is, therefore, necessary to macerate the well triturated leaves in warm (but not hot) water for some time, prior to actual distillation. To induce and accelerate splitting of the glucoside, it is advisable to add to the macerating mass a tepid infusion of powdered cherry laurel leaves. Great care has to be exercised in the industrial production of this water, as it contains substantial quantities of hydrocyanic acid which is highly poisonous (cf. Vol. II of the present work, p. 721).

As has been mentioned, distillation of the macerated leaves yields aromatic cherry laurel water. To isolate the (concentrated) essential oil, the distillation water may have to be redistilled (cohobated). The yield of oil, calculated upon the leaves, averages 0.05 per cent.

Physicochemical Properties.—Oil of cherry laurel differs from bitter almond oil chiefly in regard to odor. The physicochemical properties of the two oils are similar. Gildemeister and Hoffmann [2] reported these properties for the volatile oil of cherry laurel:

Specific Gravity at 15°	1.046 to 1.067
Optical Rotation	Mostly inactive, occasionally with a very slight rotation, +0° 12′ to −0° 46′
Refractive Index at 20°	1.539 to 1.543
Acid Number	1.6 to 2.8 (Also reported up to 10 in the same source)
Hydrocyanic Acid Content	0.4 to 4.1%, seldom higher (up to more than 8%!)
Solubility	Usually soluble in about 7 vol. of 50% alcohol; soluble in 2.5 to 4 vol. of 60% alcohol (the solubility in 60% alcohol decreases on aging of the oil); soluble in 1 to 2 vol. of 70% alcohol

Genuine oils of cherry laurel imported by Fritzsche Brothers, Inc., New York, from Southern Europe had properties varying within the following limits:

Specific Gravity at 15°/15°	1.044 to 1.067
Optical Rotation	Mostly inactive, occasionally with a slight rotation up to +0° 10′
Refractive Index at 20°	1.5417 to 1.5440
Aldehyde Content, Calculated as Benzaldehyde	82.7 to 91.2%
Hydrocyanic Acid Content	1.4 to 2.8%
Solubility	Soluble in 2.5 to 3 vol. of 60% alcohol and more

[2] "Die Ätherischen Öle," 3d Ed., Vol. II, 853.

Digitized by Google Original from CORNELL UNIVERSITY

Because of its content of hydrocyanic acid oil of cherry laurel is very poisonous and must be handled with the greatest of care.

Chemical Composition.—Tilden,[3] Fileti,[4] and Rosenthaler [5] reported the presence of the following compounds in the volatile oil derived from cherry laurel leaves:

Benzaldehyde. The chief constituent.

Hydrocyanic Acid. The poisonous component of the oil.

Nitrile of *l*-Mandelic Acid. Formerly reported to be benzaldehyde cyanohydrin, but more recently identified by Rosenthaler as the nitrile of *laevo*rotatory mandelic acid.

Benzyl Alcohol. Presence possible (Tilden).

Use.—Small quantities of oil of cherry laurel are used in certain medicinal preparations.

OIL OF *SPIRAEA ULMARIA* L.

According to Schneegans and Gerock,[1] the volatile oil distilled from the *flowers* of *Spiraea ulmaria* L. (fam. *Rosaceae*), an attractive deciduous shrub, contains *salicylaldehyde* as chief constituent, in addition to *methyl salicylate*, free *salicylic acid*, *piperonal* (heliotropin), and *vanillin*.

As regards the volatile oil distilled from the *herb*, Wicke [2] identified *salicylaldehyde*.

The oils are not produced on a commercial scale, synthetic salicylaldehyde being used instead.

[3] *Pharm. J.* [3], **5** (1875), 761.
[4] *Gazz. chim. ital.* **8** (1878), 446. Cf. *Ber.* **12** (1879), 297.
[5] *Pharm. Acta Helv.* **19** (1944), 100.
[1] *J. pharm. Elsass-Lothr.* **19** (1892), 3, 55. *Jahresber. Pharm.* (1892), 164.
[2] *Liebigs Ann.* **83** (1852), 175.

Digitized by Google
Original from CORNELL UNIVERSITY

CHAPTER II

ESSENTIAL OILS OF THE PLANT FAMILY *MYRISTICACEAE*

Digitized by Google
Original from CORNELL UNIVERSITY

OILS OF MYRISTICA

Oil of Nutmeg and Oil of Mace

Essence de Muscade and *Essence de Macis*
Aceite Esencial Nuez Moscada and *Aceite Esencial Macis*
Muskat- and *Macisöl* *Oleum Nucis Moschati* and *Oleum Macidis*

Introduction and History.—Nutmeg (myristica) and mace are both derived from the fruit of *Myristica fragrans* Houtt. (fam. *Myristicaceae*), nutmeg being the dried ripe seed, and mace the dried arillode which envelops the shell containing the seed or nutmeg. Both are very important spices, which have been used for a long time in the flavoring of savory dishes, baked goods, and other food products. They owe their characteristic aroma chiefly to the presence of an essential oil which can be isolated by steam distillation. Oil of nutmeg and oil of mace are very similar in odor and flavor, and since the nutmeg suitable for distillation is usually lower priced than mace, the former is generally employed for commercial production of the volatile oil.

According to some authors, nutmeg and mace—the latter particularly—were highly valued by the ancient Romans, who sometimes used them as a form of currency. According to other, and more reliable, sources, however, nutmeg was unknown to the Romans, becoming familiar in Europe only during the twelfth century, after it had been introduced from the East perhaps by returning Crusaders or by Arabian physicians.[1] In 1158 *"Nuces muscatarum"* imported from Alexandria were traded in the harbor of Genoa.[2] The true origin of the spice was discovered only at the beginning of the sixteenth century (in 1512) by two travelers, Barthema and Pigafetta.[3] At that time the Portuguese conquered the Moluccas, those fabled spice islands, and declared the trade in nutmeg and mace a monopoly. In 1605 the Hollanders drove the Portuguese out of the Moluccas and, taking over the spice monopoly, restricted the production of nutmeg and mace to Banda, and that of clove to Amboyna, in order to keep up prices. The monopoly of the Hollanders lasted for almost two hundred years. In 1769 the French succeeded in introducing the nutmeg tree to Ile

[1] Cf. "Nutmeg and Mace.—A Note on Their History," *Perfumery Essential Oil Record* 7 (1916), 76. Cf. *Ber. Schimmel & Co.* (1942/43), 26.
[2] Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. I, 134.
[3] G. B. Ramusio, "Delle Navigationi et Viaggi," Venice (1554), fol. 183 and fol. 389b.

Digitized by Google
Original from CORNELL UNIVERSITY

de France (now Mauritius), east of Madagascar; in 1796 Christopher Smith collected spice bearing plants in the Moluccas for the powerful East India Company. These were brought to Penang, where the first commercial crop of nutmeg and mace was gathered about 1802. This marked the end of the Dutch monopoly (which included cloves; in fact, the history of the clove trade almost parallels that of the commerce in nutmeg and mace). Early in the nineteenth century, numerous nutmeg plantations were started in many parts of Malaya and the Indonesian Archipelago, and about 1843 the tree was introduced also to Grenada in the West Indies, a small island which today produces about 40 per cent of the world's output of nutmeg and mace.

Producing Regions and Qualities.—The trade recognizes today two principal types of nutmeg (and mace), the difference between the two being based not only upon geographical origin, but also upon quality of the spice:

(1) *East Indian Nutmeg and Mace.*—According to Nijholt,[4] *Myristica fragrans* Houtt., which yields the so-called "Banda Nutmeg," is grown extensively in Indonesia, chief producing areas being the Moluccas, Minahassa (northern Celebes) and the Sangih Islands, Benkulen (West Sumatra) and Achin (North Sumatra), including the island of Nias. Throughout Indonesia nutmeg plantings are owned by natives, or occasionally by Chinese.

According to Landes,[5] there are four grades of East Indian nutmegs:

(a) The "Banda Nutmegs," considered perhaps the finest for commercial use, and containing about 8 per cent of essential oil.

(b) The "Siauw Nutmegs," considered almost as good as the "Banda," but containing only about 6.5 per cent of essential oil.

(c) The "Penang Nutmegs." Prior to World War II, these were of good quality; but they are now wormy and moldy beyond the possibility of reconditioning, probably as a result of neglecting plantations during the war, and can be used only for distillation purposes.

(d) The "Papua Nutmegs." These are among those nutmegs not derived from *Myristica fragrans* Houtt., but from an allied species, viz., *Myristica argentea* Warb. They can easily be recognized by their shape and peculiar, unpleasant odor. Papua nutmegs have been imported into the United States only since the last war. They should not be used for distillation, the yield of oil being low, and the oil possessing an odor reminiscent of sassafras.

In addition to the four above-mentioned grades, there is, perhaps, a fifth

[4] Private communication from Dr. J. A. Nijholt, Director of the Laboratorium voor Scheikundig Onderzoek, Buitenzorg, Java.

[5] Private communication from Dr. Karl H. Landes, New York.

Digitized by Google Original from CORNELL UNIVERSITY

grade, the so-called "Java Estate Nutmegs," small quantities of which enter the United States market. They are of very good quality and may be classified as an intermediate between the "Banda" and the "Siauw" nutmegs.

As was pointed out above, the "Papua" nutmegs are derived from a species of *Myristica* other than *fragrans* Houtt. Whether this is the case also with some of the other grades lower than the "Banda" cannot easily be ascertained. *Myristica succedanea* Bl., in Indonesia called "Pala Maba," e.g., produces a grade of nutmeg and mace which is only slightly, if at all, inferior to the first grade "Banda" spice. (The oils derived from species of *Myristica* other than *fragrans* Houtt. will be described in separate monographs. The present monograph will deal exclusively with the oils of nutmeg and mace from *Myristica fragrans,* both East Indian and West Indian.)

As regards the grades of mace produced in East India, Landes [6] distinguishes between the following:

(a) The "Banda Mace," considered the finest. This is prepared for the market with more care than any other grade of mace, being artificially dried and fumigated in specially constructed dryers and carefully sifted. Any broken pieces are eliminated. The color is bright orange, the aroma very fine.

(b) The "Java Estate Mace," grown near Semarang, in Java. Like the "Banda," this is artificially dried, and quite free of insect infestation. It can easily be recognized by its round shape and its gold-yellow color, interspersed with brilliant crimson streaks.

(c) The "Siauw Mace," originating from the islands of Celebes, Ternati, Talanda, and Sangi. The color is lighter than that of the "Banda"; the brighter the color, the higher the price. Depending upon color and size, the Siauw mace is classified as of No. 1 and No. 2 quality. Broken pieces are classified as siftings. In general, Siauw mace contains about 10 per cent less volatile oil than the Banda mace.

(d) The "Papua Mace," derived from *Myristica argentea* Warb. This type is entirely unsuitable for the purposes of grinding or distilling, since it contains a high percentage of fatty oil and comparatively little essential oil. (The latter exhibits an undesirable turpentine-like aroma.)

The above-mentioned grades of East Indian mace contain, on the average, the following quantities of volatile oil:

	Per Cent
"Banda Mace"	13
"Java Estate Mace"	11 to 12
"Siauw Mace"	10 to 11
"Papua Mace"	4

[6] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

West Indian mace (which will be described below) yields from 8 to 9 per cent of essential oil.

Nijholt [7] reported the following figures for nutmeg and mace exports from Indonesia in the years 1936 to 1940 inclusive, and 1948, in metric tons:

	Nutmeg	*Mace*
1936	4,192	777
1937	4,415	823
1938	3,977	834
1939	4,215	810
1940	3,612	847
1948	2,676	494

Shelled nutmegs are usually shipped directly from the harbors near the producing regions to the consuming countries. Singapore does not handle much of this type. However, of the unshelled nutmegs, about 75 per cent of those produced first go to Singapore for transshipment abroad.

In 1938 a total of 435,867 kg. of nutmegs ("distillers grade") was exported from Macassar (Banda). These exports were distributed as follows: [8]

	Kilograms
United States	389,451
Holland	15,345
Holland, Option	6,131
Great Britain	11,528
Great Britain, Option	5,120
Germany	8,292
	435,867

According to Swing,[9] the nutmeg tree was introduced to Ceylon in 1804, and now grows on the island in deep loamy soil, up to an elevation of 2,500 ft. In 1946 Ceylon exported 1,063 hundredweights of nutmeg, in 1947 the exports amounted to 1,488 hundredweights.

(2) *West Indian Nutmeg and Mace.*—Until 1939 the West Indies produced only about one-sixth of the world's supply of nutmeg and mace, but since the outbreak of World War II (when the spice from the East Indies became unavailable) production in the West Indies has increased to about 40 per cent of the world's output. The bulk of the West Indian nutmeg and mace originates from the small British island of Grenada, one of the Windward Islands, lying just to the north of Trinidad. Before World War

[7] Private communication from Dr. J. A. Nijholt, Director of the Laboratorium voor Scheikundig Onderzoek, Buitenzorg, Java.
[8] *Ber. Schimmel & Co.* (1939), 53.
[9] *Spice Mill* **72**, No. 2 (1949), 48.

Digitized by Google Original from CORNELL UNIVERSITY

II the West Indian spice was shipped largely to Great Britain and continental Europe, but during the war the picture changed and the United States became the principal buyer of the West Indian nutmeg.

According to Whitaker,[10] the nutmeg tree was introduced into Grenada about 1843, when the captain of a visiting Dutch ship gave one of Grenada's planters a few of the many nutmeg seeds he was bringing to the Netherlands from the island of Banda in Indonesia. These seeds produced tall, sturdy trees, which flourished in the soil and climate of Grenada. They formed the core of a new industry, which in later years came to provide employment for half of the island's population. As practically all of Grenada's nutmegs and mace are exported, the following table of exports for the years 1940 to 1945 may also be considered as production or crop figures:

Year	*Total (in tons)*	*United Kingdom (in tons)*	*Canada (in tons)*	*United States (in tons)*	*Other (in tons)*
Nutmegs					
1940	2,095	523	128	1,331	113
1941	1,910	700	144	1,015	51
1942	1,876	780	102	921	73
1943	2,270	351	80	1,636	203
1944	2,574	224	110	1,935	305
1945	2,341	500	73	1,553	215
Mace					
1940	274	222	31	20	1
1941	324	302	18	3	1
1942	340	288	10	34	8
1943	334	71	14	223	26
1944	338	41	22	233	42
1945	338	92	24	158	64

According to Landes,[11] the quality of the West Indian nutmegs has been gradually but steadily improving. Shipments now usually meet standards, and lots are rarely rejected because of worminess or an excessive amount of moisture. Recent shipments of West Indian nutmegs have shown a content of volatile oil as high as 9 per cent, which is greater than that of Banda nutmegs from Indonesia. The reason may lie in the fact that many of the nutmeg trees of Grenada have now reached an age of thirty to thirty-five years, i.e., the prime of their productivity.

As regards West Indian mace, its quality is still below that of the East Indian spice, and only the price difference between the two products has

[10] *U. S. Dept. Commerce, Foreign Commerce Weekly,* Washington, D. C., **25** (November 23, 1946), 8.

[11] Private communication from Dr. Karl H. Landes, New York.

Digitized by Google Original from CORNELL UNIVERSITY

compelled some of the grinders to substitute the West Indian for the East Indian mace. The former possesses a nice yellow color, but its texture is brittle, and its volatile oil content (8 to 9 per cent) below that of the East Indian mace. Moreover, the volatile oil exhibits a turpentine-like aroma.

Botany.—*Myristica fragrans* Houtt., one of about 100 known *Myristica* species,[12] is a bushy tree with numerous spreading branches; it attains a height of 30 to 40 ft., in some cases even 60 ft. In its general appearance the nutmeg tree resembles an orange tree. According to Ridley,[13] the trees are in most cases unisexual, bearing male flowers or female flowers only, but it is not uncommon to find a tree with flowers of both sexes upon it. It has long been known that a male tree after some years, usually about six, frequently commences to produce female flowers, and eventually becomes wholly female. The fruit appears on the tree mingled with flowers; in other words the nutmeg tree, like the lime tree, bears flowers and fruit at the same time. The orange-yellow, smooth fruit, when ripe, is one of the most beautiful in nature. A pendulous, fleshy drupe of quite variable form, it is globular on some trees, oval or pear-shaped on others. The size varies, but averages 2.5 in. In general, the fruit resembles a small peach. The husk (pericarp) is of fleshy, somewhat firm texture, and about 0.5 in. thick. It contains an acid, astringent juice with an aromatic flavor of nutmeg. When ripe, the fleshy husk opens by splitting into two halves, from the top nearly to the base, along the groove which runs down one side. On splitting of the husk, the nut appears. It has a deep brown, glossy seed coat or shell that contains the seed. The latter, when dried, is the nutmeg of commerce. The seed coat is partly covered by a peculiar, net-like and crimson, leathery arillode, growing from the base of the seed. The dried arillode is the mace of commerce.

The shell (*testa*) has a woody and brittle consistency; when dried it can easily be cracked to remove the seed (after the arillode has been peeled off the shell by hand). Within the shell a sound seed should measure about 1 in. in diameter. When fresh, the oval seed nearly fills the shell, but on drying, the seed (nutmeg) shrinks somewhat and then rattles within the shell. Seed used for sowing should not be dry enough to rattle, but for trade purposes the nutmegs should rattle in the shell when shaken. A dried, sound nutmeg, removed from the shell, is hard and woody in texture, ovoid or ellipsoidal in form, from 20 to 30 mm. in length and about 20 mm. in thickness, light brown to dark brown in color, reticulately furrowed. When cut, the inside shows a waxy and oily luster, with brown spots on a

[12] There are, however, a few others, the nuts of which are slightly aromatic, and occasionally collected by natives and exported to Europe, more as adulterants of true nutmeg rather than for separate use.

[13] "Spices," London, Macmillan & Company, Ltd. (1912), 94.

Digitized by Google Original from CORNELL UNIVERSITY

grayish ground. The dried seed (nutmeg) contains from 5 to 15 per cent of volatile oil, from 25 to 40 per cent of fixed oil, and from 5 to 15 per cent of ashes; the balance consists of moisture, fiber, and starch.

Mace (the arillode enlacing the shell of the seed), when freshly removed, exhibits a bright red color which, however, changes to orange-yellow on drying. It is marketed in the form of irregularly shaped pieces which swell when immersed in water. Odor and flavor are similar to, yet distinctly different from those of nutmeg. Mace contains from 4 to 14 per cent of a volatile oil closely resembling that derived from nutmegs. West Indian mace has a paler color than the East Indian and is less aromatic.

Production of Nutmeg and Mace in the East Indies.—The nutmeg tree flourishes on a variety of soils, except on bare clay slopes, sandy, or waterlogged soils. The best altitude is from sea level to about 1,000 ft. The tree requires a hot, moist climate and appears to prefer proximity to the sea. Rainfall should be from 80 to 100 in. per year, well spread over the different months, with no absolutely dry spells of more than four to five days, and no continuous rains, without sun, of more than a fortnight. During wet spells parasitic fungi are most active.

According to Ridley,[14] carefully chosen, well-formed seed should be planted within 24 hr. of gathering, if possible, in beds of good soil, well dug over, manured and drained. The seed should be placed from 12 to 18 in. apart in rows, and at a depth of about 2.5 in. The beds need shading under a roof loosely made of leaves, admitting a certain amount of light. The beds should be watered every other day. The seeds require from four to six weeks to germinate, and sometimes longer. The young plants remain in the nursery until they are about 6 in. tall, i.e., for about six months. Then they have to be transplanted, during the rainy season, to their permanent position in the field, at a distance of 26 to 30 ft. apart, either in lines or in quincunx arrangement. The planting holes should be about 4 ft. wide, and at least 3 ft. deep. In hot places the young plants need a certain amount of shading until they have settled in the ground and begun to push out their roots. Being in its natural state a jungle plant, the nutmeg tree grows better and remains healthier when partly shaded (e.g., by the well-known "rain tree" *Pithecolobium saman*), than when fully exposed to the hot sun.

The tree does not flower until the eighth or ninth year, after which it bears flowers and fruit together for many years. The nutmeg tree is normally monoecious, i.e., either male and bearing only male flowers, or female and bearing only female ones. Obviously, only the female flowers produce fruit, but a small proportion of male trees (about one in ten) is required to

[14] *Ibid.*, 107.

Digitized by Google Original from CORNELL UNIVERSITY

provide the pollen necessary to fertilize the flowers on the female trees. Native growers, therefore, usually exterminate most of the male trees as soon as the trees have sufficiently developed to show their flowers and so become distinguishable. This, however, is possible only about seven years after planting. More progressive growers then head down any superfluous male trees and graft them with scions of female plants.

The trees commence to fruit usually in the eighth or ninth year, but reach their prime of productivity only when about twenty-five years old. They bear well up to sixty years, or even longer. The fruits ripen about six months after the flowering period. The fruit is ripe when it splits and shows the shell of the seed enlaced with its brilliant red mace. The fruits are sometimes allowed to drop to the ground; nuts and attached mace are then picked up daily and collected in baskets. The usual practice, in Indonesia, however, is to pull the fruit off the branches by hand, using hooked staffs to reach fruit on lofty branches. A good worker can collect from 1,000 to 1,500 nuts a day.

The yield of nutmeg and mace per tree varies considerably. A healthy tree should average 1,500 to 2,000 nuts per year. As regards weight, each tree should produce 10 lb. of nutmegs to 1 lb. of mace; some trees give much more than this (Ridley).

The tree bears fruit more or less all the year round, but in most places the heaviest crops are obtained in May and June, and again in August and September.

After arrival of the collected material at the working shed the mace (arillode) is detached from the shell of the seed with a knife, or simply by hand, by opening it from the top of the shell and reflexing it. The mace is attached to the seed only by its base, known as the heel of the mace. The freshly removed mace is flattened out by hand, spread on bamboo trays or on mats, and dried in the sun from 4 to 5 hr. a day for a fortnight. During dry weather drying may be accomplished in two or three days. Before nightfall the trays or mats must be brought into a drying-shed, to prevent wetting of the material by dew. Great care must be exercised to prevent the mace from getting moldy, which may easily happen. When fresh, the mace possesses a brilliant red color; on drying this changes to orange, and after a few months to yellow.

According to Ridley,[15] a perfect sample of mace should consist of entire double blades (not broken), flattened and of large size, horny in texture, not too brittle, and of good, clear and bright color.

After removal of the mace the nuts are placed on trays and exposed to the sun for several weeks until dry. Often drying is completed over a slow

[15] *Ibid.*, 146.

Digitized by Google Original from CORNELL UNIVERSITY

charcoal fire in a drying-house, care being exercised not to raise the temperature too high, as the seed will then shrivel and diminish in value. The seeds are dried while still in the shell (the thin, brittle outer coating, or *testa*) because otherwise they are attacked by beetles. Drying is completed when the seed rattles within the shell. When the seeds are sufficiently dry, the shells must be removed; this is usually accomplished by hitting them on the end (not on the side!) with a wooden club or mallet. Machines for cracking of nutmegs have been invented and are used on some of the large estates. Once the seed has been removed from the shell, it is exposed to the attacks of all kinds of beetles, especially while stored in the warehouse ("godown"). The beetles deposit eggs in the seed, and the larvae bore holes into it, destroying part of it. Most of these beetles are pests common in the godowns, attacking all kinds of food products. Therefore, the godowns should be thoroughly cleaned from time to time. To prevent damage by insects, the nutmegs are often limed at the place of production. In some parts of Indonesia this is done by sprinkling the dried nutmegs profusely with powdered lime, or by rubbing each nut individually with the chemical, or by dipping them into a mixture of lime and water. At one time, fumigation with sulfur dioxide was occasionally practiced, but this has now been largely abandoned. A more recent method is fumigation of the nutmegs with methyl bromide, in special chambers. However, at the present time, most of the Indonesian product reaches the world markets untreated.

On arrival at the warehouse, the nutmegs are tested by sounding. This is done simply by bouncing them individually on an iron plate. The assorter can thus detect worm-eaten and damaged specimens, which he removes. Sound nutmegs are assorted according to their size and number per pound. At the time of the author's visit to Malaya and Indonesia, just prior to the outbreak of World War II, nutmegs were classified as follows:

(a) Whole, sound nutmegs. These ranged from 60 to 125 nutmegs per pound, the greatest demand being for 85 to 95 nuts per pound. They were known as "Large" (60 to 80 per lb.), "Medium" (85 to 95 per lb.), and "Small" nutmegs (100 to 125 per lb.), and were sold to the spice trade.

(b) Sound shrivels. A quality much in demand for grinding.

(c) Rejections. Because of their low price, these are suitable for distillation.

(d) Broken and wormy. The quality most suitable for distillation because of the low content of fatty oil. Prior to World War II large quantities were shipped to Europe, particularly to Hamburg. The United States permits entry of this grade only under condition that the material be used exclusively for distillation.

Production of Nutmeg and Mace in the West Indies.—As has been mentioned, the nutmeg tree was introduced to Grenada about 1843, when a

Digitized by Google Original from CORNELL UNIVERSITY

Dutch ship bringing spices from Indonesia to Holland called on this small island in the West Indies.

According to Whitaker,[16] in the Windward Islands the trees appear to grow best at an elevation ranging from 500 to 1,500 ft. above sea level, in areas where the rainfall is fairly constant throughout the year. A large part of the fertile mountain slopes of Grenada above 800 ft. elevation is covered with dense groves of nutmeg trees. These trees grow very close together on the steep hillsides, forming an almost unbroken canopy above the ground. The hillsides slope so sharply that mechanical cultivation cannot be practiced; hence the trees do not have to be set out in lines. They are simply planted wherever there appears to be ample room for them to grow.

According to Noel,[17] the principal factor influencing the growth of the nutmeg tree is the amount of rainfall which should be well distributed and at least 80 in. per year. Optimum conditions in this respect prevail at elevations of from 600 to 800 ft., in the center of the island. The tree does not grow in the coastal plains.

Nutmeg trees bear the first fruit four years after planting, but the first commercial harvest takes place only after sixteen years. The trees continue bearing fruit for a hundred years and perhaps more.

It is estimated that there are about 10,000 acres devoted to the cultivation of nutmegs in Grenada. Large plantations comprise approximately 70 per cent of this acreage, the remaining 30 per cent being plots of from 1 to 5 acres in the hands of small farmers. Out of a population of 70,000, about 14,000 are such farmers.

Whereas in the Far East the fruits are usually picked from the tree before the husk splits, in Grenada the husk is allowed to split while the fruit is still on the tree, and the ripe fruit is collected from the ground. If the fruits are not picked up quickly, the nutmegs become waterlogged and ferment or start to grow, and weevils and worms enter the shell.

Nutmeg trees produce fruit all year round, but most heavily in August and September, and from February to April, inclusive. In June, November, and December collections are lightest. The productivity of a tree depends upon ecological (primarily soil) conditions and upon its vigor (plant selection). According to information gathered by the author during a visit to Grenada, the yield ranges from a few pounds of dried nutmegs to as many as 100 lb. per tree. Whitaker[18] reports that in Grenada the trees average

[16] *U. S. Dept. Commerce, Foreign Commerce Weekly,* Washington, D. C. **25** (November 23, 1946), 7. Cf. *Spice Mill* **71**, No. 5 (1948), 51.

[17] Author's conversation with Mr. Carlyle Noel, Grenville, Grenada, and Mr. William O'Brien Donovan, St. George, Grenada.

[18] *U. S. Dept. Commerce, Foreign Commerce Weekly,* Washington, D. C. **25** (November 23, 1946), 7. Cf. *Spice Mill* **71**, No. 5 (1948), 51.

Digitized by Google Original from CORNELL UNIVERSITY

about 1,000 nutmegs per year and that a tree in full bearing produces about 50 lb. of green nutmegs per year. An acre of nutmeg trees contains perhaps 90 or 100 trees. Many of these are young, not yet in full bearing or indeed not bearing at all, and some are past their prime. On a number of estates the less prolific young trees are cut out from time to time. The return per acre averages 1,500 lb. of green nutmegs a year—which, when dried and removed from the shells, yield about 720 lb. of sound nuts.

The yield of mace averages 150 lb. of green, or 30 to 40 lb. of cured, mace per acre. Ordinarily it takes about 100 lb. of green nutmegs to yield 8 lb. of fresh mace.

Total yearly production of nutmegs in Grenada averages 6,000,000 lb., that of mace 600,000 lb.

The Grenada Co-Operative Nutmeg Association advises its members never to collect or harvest the fruit prior to the natural opening of the "husk," considering it an absolutely unsound policy to "reap" fruit from the trees. Only fully ripened fruit fallen to the ground should be gathered, and this, under favorable weather conditions, within 24 hr. after their fall. Immature nutmegs result in a very low-grade spice. The work of collecting the fruit is done only once a day by women and children who go through the orchards. The gathered fruit (or the nutmegs for that matter) should never be heaped, as this may cause fermentation or sweating of the nutmegs and mold development. The soft husk is removed from the core, and the mace separated from the shell containing the nutmeg. Mace and nutmegs (the latter still within their shells) are then placed in separate baskets and brought to the "boucans" (curing houses) for drying. Here women flatten the pieces of mace and later spread them about 1 in. deep on large trays to dry in the sun for about 48 to 60 hr. When thoroughly dried, the mace—now reddish-brown and brittle—is packed away in large bins measuring about 6 ft. in each direction, where it is sealed tightly and kept from the ravages of the mace weevil by regular carbon bisulfide fumigation. A few teaspoonfuls of this chemical placed in a little saucer in the top of the bins every few days keep insects and mice away. After about five months the mace turns to a deep yellow color, about the shade of flint corn. At this stage it is ready to be prepared for export. For this purpose it is taken out of the storage bins and assorted by hand. In the cleaning process, mace is first sifted in a large mechanical oscillating sifter, then picked over by women experienced in this work. The large clear yellow pieces constitute the highest grade, or "pale whole mace." The darker colored pieces, somewhat smaller in size, are classified as "No. 1 broken grade," the small, dark-colored pieces as "No. 2 broken." Chaff and dark bits, stained from lying too long in the fields or in water, or which have some malformation, are put aside as an inferior type—"mace pickings"—

Digitized by Google Original from CORNELL UNIVERSITY

and seldom sold in the United States. After being sorted, mace is packed by hand according to grade in light plywood cases similar to tea chests, each containing 200 lb.

As regards nutmegs, they are dried (cured) while still enclosed in their shiny dark-brown shells, then removed (by cracking) from the shells, but only on orders for shipment of the spice. This helps to protect the kernels (nutmegs) against infestation by insects. As a general rule, the nuts are best cured in the air and away from sunshine, but such a procedure can be carried out only in buildings with an efficient system of aeration. The nuts are placed on shallow trays under cover, being spread no deeper than 3 in.; if spread more thickly they are liable to ferment or cure improperly. Some drying frames are 20 ft. long and 10 ft. wide; the drying sheds or "boucans" may be as large as 60 to 80 ft. long and 30 ft. wide. During the drying the nuts must be stirred two or three times a day with a long-handled hoe, to insure proper ventilation. A good product can be obtained in six weeks' time if only freshly fallen fruits are gathered within 24 hr. of their fall, and cured in the manner now usually employed, viz., aired for seven days; then exposed to early morning sunshine until about 9:30 A.M.—this for ten days; then to daily sunshine in the morning until not later than 11:30 A.M., and in the afternoon for about 1½ hr., until 5 P.M.—this for fourteen days; and finally ½ hr. of sunshine every morning—this for twelve days (with turning twice daily for each of these treatments). After about six weeks of curing, the dried nuts are shoveled into bags and stored in a clean, well-ventilated place to await shipment. In this stage the nutmeg is still enclosed in its shell, approximately a quarter of an inch longer and wider than the kernel (nutmeg) itself. Just prior to shipment, the nuts are taken out of the bags, one bag at a time, and dumped on a clean wooden floor. Women with small wooden hammers rapidly crack the shells surrounding the kernels. The nutmegs are then dumped into tanks filled with water, and slowly stirred. Those floating are considered "grinders" or "defectives," and employed for distillation purposes; nutmegs that sink to the bottom of the tank are considered "sound, unassorted" nutmegs, suitable as food. Both types are thoroughly dried in the air, carefully picked over, and finally exported from St. George, the only shipping port on the island of Grenada. Export of the spice is now a monopoly of the Grenada Co-Operative Nutmeg Association, with headquarters in St. George.

For shipment to England, Grenada nutmegs are graded in 60's, 65's, 80's, 110's and 130's—these numbers referring to the quantity of nuts per pound. When shipped to the United States they are not graded for size, but simply divided into two classes, "sound" nutmegs (used principally in food), and "defectives" (employed only for the distillation of nutmeg oil).

Digitized by Google
Original from CORNELL UNIVERSITY

All nutmegs imported into the United States must meet standards set by the Pure Food and Drug Administration. The bulk of nutmeg oil produced in Europe and in the United States is derived from imported spice. However, a few years ago Grenada began local distillation of small quantities. Since nutmegs are available for the entire year, the oil is distilled at all seasons from both the shells and defective nuts. In 1946 there was only one still on the island for the distillation of nutmeg oil, but production could be largely increased by using rum stills or importing other stills. This would allow utilization of nutmeg shells, now a waste product. The bulk of nutmeg oil produced in Grenada goes to England. In 1945 about 3,400 lb. of oil were produced on the island; of this quantity 2,584 lb. went to the United Kingdom and 540 lb. to the United States. In 1946 the exports of nutmeg oil from Grenada amounted to 7,065 lb.[19]

The Fixed Oil.—Among other constituents nutmegs contain from 25 to 40 per cent of fixed oil, also known as concrete or expressed oil, or nutmeg butter (*Oleum myristicae expressum*). This is an orange-colored mass, very aromatic and of butter-like consistency at room temperature. The oil can be obtained by expressing crushed nutmegs between heated plates in the presence of steam, or by extracting with a volatile solvent.

Power and Salway [20] found that fixed oil of nutmeg contains 73 per cent of trimyristin (glyceryl myristate), 12.5 per cent of essential (volatile) oil, 3.5 per cent of fat (glyceryl oleate and linoleate), 2 per cent of resin, minute quantities of formic, acetic and cerotic acids, and 8.5 per cent of unsaponifiable residue.

The fixed oil is of no culinary interest, but may be used to a limited extent in medicinal preparations, particularly in mild stimulants for external application. According to Redgrove,[21] the fixed oil was at one time highly favored for the preparation of certain hair tonics.

It should be mentioned here that it is very difficult to remove the volatile oil from the fixed oil by distillation: the latter oil retains the volatile oil quite tenaciously through reduction of vapor pressure and vaporization rate (cf. Vol. I of the present work, p. 162).

The Volatile (Essential) Oil.—As was mentioned above, both nutmeg and mace contain a volatile oil which can be isolated by steam distillation. The yield of oil varies greatly with the geographical origin of the spice and with its quality; hence it is difficult to give average figures. Wormy nutmegs, e.g., in commercial distillation give a much better yield of volatile oil than do sound nutmegs, for the simple reason that in the former most of the fixed (fatty oil) has been devoured by the worms, while the strongly aro-

[19] *Bull. Imp. Inst.* **46** (1948), 167, 173.
[20] *J. Chem. Soc.* **93** (1908), 1653.
[21] "Spices and Condiments," London, Pitman and Sons, Ltd. (1933), 295.

Digitized by Google Original from CORNELL UNIVERSITY

matic volatile oil remains intact. Sound nutmegs, on the other hand, retain all their fixed oil, and the latter, on distillation, tends to retain the volatile oil, thus lowering its yield (see above).

In odor, flavor, physicochemical properties and chemical composition, the volatile oils of nutmeg and mace are so similar that the trade usually draws no distinction between them. Since mace is generally more expensive than nutmeg (particularly broken and wormy nutmeg), the essential oil is produced mostly from the latter, and only seldom from mace.

Distillation and Yield of Oil.—Prior to distillation, the nutmegs must be comminuted, and if *sound* nutmegs are to be used, most of the fixed oil must be removed by expression. In this latter event, however, the fixed oil will dissolve much of the volatile oil present in the nuts, and on distillation of the chopped and pressed nutmegs a low yield of volatile oil will be obtained. A more suitable, and incidentally much more economical, raw material is therefore the quality known in the trade as "broken and wormy," consisting of refuse and low-priced nutmegs, from which worms have removed much of the fixed oil.

Clevenger [22] found that shriveled East Indian nutmegs give a much larger percentage of volatile oil than do the mature sound ones. The same author also observed that the loss of volatile oil from *ground* mace or nutmegs is relatively rapid, amounting to approximately 80 per cent in two months. For this reason the material should be distilled immediately after grinding.

Gildemeister and Hoffmann [23] reported a yield of volatile oil ranging from 7 to 16 per cent for nutmegs, and from 4 to 15 per cent for mace. In the author's own experience, the yield of oil depends greatly upon the origin, condition, and age of the spice; in the case of nutmegs it varies between 6 and 16 per cent. Mace gives about 10 per cent of volatile oil.

Distillation of the comminuted material is best carried out with live steam; cohobation of the distillation waters may be necessary. With a low pressure steam, about 80 per cent of the oil distills during the first 2 hr.; the balance of the oil requires up to 10 hr. to distill over. High-pressure or superheated steam should not be employed as it carries over some of the fixed oil present in the spice.

Physicochemical Properties of Oil of Nutmeg

Oil of nutmeg is a mobile, almost colorless or pale yellow liquid, possessing an odor and flavor characteristic of the spice, especially on dilution. With the passage of time the oil takes up oxygen and partly resinifies, becoming more viscous.

[22] *J. Assocn. Official Agr. Chem.* **18** (1935), 611.
[23] "Die Ätherischen Öle," 3d Ed., Vol. II, 596.

Digitized by Google Original from CORNELL UNIVERSITY

The physicochemical properties vary within quite wide limits, depending upon the origin and quality of the spice and the method of distillation. Thus the properties of the oils derived from East Indian nutmegs differ substantially from those of the oils distilled from West Indian nutmegs. Compared with the first, the West Indian type of oil exhibits a lower specific gravity, refractive index, and evaporation residue, and a higher optical rotation. This is the result chiefly of the predominance of terpenes in the West Indian oil. For the same reason the odor and flavor of the East Indian oil are much more pronounced and more characteristic of the spice than those of the West Indian type. The United States Pharmacopoeia, Fourteenth Revision, admits both oils, but requires that the label indicate whether the myristica (nutmeg) oil is of East Indian or West Indian origin.

A. East Indian Oil.—Gildemeister and Hoffmann [24] reported these properties for nutmeg oils, apparently of East Indian origin:

Specific Gravity at 15°	0.865 to 0.925
Optical Rotation	+8° 0′ to +30° 0′
Refractive Index at 20°	1.479 to 1.488
Acid Number	Up to 3.0
Ester Number	2 to 9
Ester Number after Acetylation	25 to 31
Solubility	Soluble in 0.5 to 3 vol. of 90% alcohol
Evaporation Residue	1 to 1.5 per cent, if 5 g. of oil are slowly evaporated for 12 to 15 hr., until the weight of the evaporation residue is constant
Boiling Range	On distillation in a fractionation flask, about 60 per cent of the oil distills below 180°

Genuine East Indian nutmeg oils distilled by Fritzsche Brothers, Inc., New York, from imported nutmegs of various quality, had properties ranging within the following limits:

Specific Gravity at 25°/25°	0.880 to 0.913
Optical Rotation	+7° 53′ to +22° 10′, usually above +10°. Several lots of old nutmegs produced oils having abnormally low rotations, as low as +4° 46′
Refractive Index at 20°	1.4776 to 1.4861
Evaporation Residue	0.3 to 2.1%
Solubility at 20°	Soluble in 1 to 2.5 vol. and more of 90% alcohol

As regards the evaporation residue of the oil and method of determination, see Vol. I of the present work, pp. 259, 260.

[24] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

Clevenger [25] reported these properties for a number of oils distilled from Banda nutmegs (I), Padang nutmegs (II), and shriveled East Indian nutmegs (III):

	I	*II*	*III*
Yield of Oil (cc. per 100 g. of spice)	4 to 10	8 to 11.5	11.5 to 21.0
Specific Gravity at 20°/20°	0.919 to 0.956	0.878 to 0.909	0.897 to 0.916
Optical Rotation at 20°	+11° 42′ to +20° 36′	+20° 42′ to +27° 42′	+19° 18′ to +21° 48′
Refractive Index at 20°	1.483 to 1.495	1.476 to 1.481	1.479 to 1.482
Acid Number	2.5 and 8.8	1.2 and 2.4	2.46
Ester Number	13.8 and 19.7	6.0 and 11.2	12.3

Clevenger [26] arrived at the conclusion that the volatile oils obtained from ground nutmegs and mace that have been exposed in the laboratory exhibit a definite increase in specific gravity, refractive index, acid and ester numbers, and a distinct decrease in optical rotation. These observations should prove valuable in determining the conditions under which these products are to be handled.

Distilling *fresh* (undried) East Indian nutmegs, de Jong [27] obtained an oil with the following properties:

Specific Gravity at 26°	0.940
Optical Rotation at 26°	+10° 20′
Boiling Range at atm. pr.	155° to 175°—9.5%
	175° to 200°—37%
	200° to 250°—22.0%
	250° to 285°—27.0%

An experimental distillation, on a commercial scale, of Ceylon nutmegs by Fritzsche Brothers, Inc., New York, gave an oil with the following properties:

Specific Gravity at 25°/25°	0.873
Optical Rotation	+28° 55′
Refractive Index at 20°	1.4765
Evaporation Residue	1.0%
Solubility	Soluble in 3 vol. of 90% alcohol and more

B. West Indian Oil.—Genuine West Indian nutmeg oils distilled by Fritzsche Brothers, Inc., New York, from imported nutmegs of various quality, had properties ranging within these limits:

[25] *J. Assocn. Official Agr. Chem.* **18** (1935), 614.
[26] *Ibid.*
[27] *Teysmannia* (1907), No. 8. Cf. *Ber. Schimmel & Co.*, October (1908), 91.

Digitized by Google Original from CORNELL UNIVERSITY

Specific Gravity at 25°/25°	0.859 to 0.865
Optical Rotation	+25° 45′ to +38° 32′
Refractive Index at 20°	1.4729 to 1.4746
Evaporation Residue	0.2 to 0.8%
Solubility at 20°	Soluble in 2 to 3 vol. of 90% alcohol and more

Clevenger [28] reported the following properties for a number of oils distilled from West Indian nutmegs:

Yield of Oil (cc. per 100 g. of spice)	8.5 to 10.0
Specific Gravity at 20°/20°	0.859 to 0.868
Optical Rotation at 20°	+40° 48′ to +49° 48′
Refractive Index at 20°	1.469 to 1.472
Acid Number	1.0 and 1.3
Ester Number	6.8 and 7.3

According to Clevenger,[29] West Indian nutmegs and mace yield volatile oils which may be distinguished from the corresponding East Indian oils by their low specific gravities and refractive indices, and high optical rotations.

Nutmegs imported from Grenada (B.W.I.) and distilled in the Imperial Institute, London,[30] yielded about 11 per cent of volatile oil with these properties:

	I	*II*
Specific Gravity at 15.5°/15.5°	0.8666	0.8682
Optical Rotation at 25°	+48° 42′	+48° 24′ (at 24°)
Refractive Index at 20°	1.4728	1.4736
Solubility at 15.5°	Soluble in 4 vol. of 90% alcohol, with slight opalescence	

These properties demonstrate that the West Indian nutmeg oils differ markedly from the East Indian oils. The odor of the former is weaker, less characteristic and spicy than that of the East Indian oils. This difference results from the fact that West Indian oils contain a larger amount of terpenes, which lower their quality.

Physicochemical Properties of Oil of Mace

Odor and flavor, as well as physicochemical properties of mace oil, closely resemble those of nutmeg oil (see above). On exposure to the air, the oil partly resinifies and takes on a turpentine-like, rather disagreeable odor.

[28] *J. Assocn. Official Agr. Chem.* **18** (1935), 613.
[29] *Ibid.*, 615.
[30] *Bull. Imp. Inst.* **35** (1937), 289.

Digitized by Google Original from CORNELL UNIVERSITY

A. East Indian Oil.—Gildemeister and Hoffmann [31] reported the following properties for mace oils, apparently of East Indian origin:

Specific Gravity at 15°	0.890 to 0.930
Optical Rotation	+10° 0′ to +22° 0′
Solubility	Clearly soluble in 2 to 3 vol. of 90% alcohol

Distilling East Indian mace from Banda (I) and from Padang (II), Clevenger [32] obtained volatile oils with these values:

	I	*II*
Yield of Oil (cc. per 100 g. of spice)	10.4 to 16.4	17.0 to 27.0
Specific Gravity at 20°/20°	0.923 to 0.947	0.917 to 0.936
Optical Rotation at 20°	+2° 42′ to +11° 48′	+7° 36′ to +11° 24′
Refractive Index at 20°	1.486 to 1.494	1.485 to 1.491
Acid Number	2.0 to 3.9	1.4 to 3.0
Ester Number	1.2 to 7.3	3.5 to 8.5

Clevenger [33] noted that volatile oils distilled from mace exhibit a lower dextrorotation than oils derived from nutmegs of corresponding geographical origin. This may be the result of the loss, in mace, of the more volatile fractions of oil, which have a high dextrorotation.

B. West Indian Oil.—Clevenger [34] also distilled a number of oils from West Indian mace and reported the following properties:

Yield of Oil (cc. per 100 g. of spice)	8.5 to 15.0
Specific Gravity at 20°/20°	0.860 to 0.892
Optical Rotation at 20°	+21° 18′ to +41° 30′
Refractive Index at 20°	1.472 to 1.479
Acid Number	1.5 to 6.2
Ester Number	2.8 to 12.8

As in the case of the nutmeg oils, the West Indian mace oils exhibited lower specific gravities and refractive indices and higher optical rotations than the East Indian mace oils. Odor and flavor of the former type of oil are inferior to those of the East Indian oils.

Chemical Composition of Nutmeg and Mace Oil

Oils of nutmeg and mace are so similar that their chemical composition can be discussed in one section. In fact, a number of researchers in the past did not clearly define the origin of the oil which they examined.

The earliest investigations of nutmeg (or mace) oil date back to the first

[31] "Die Ätherischen Öle," 3d Ed., Vol. II, 597.
[32] *J. Assocn. Official Agr. Chem.* **18** (1935), 614.
[33] *Ibid.* [34] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

decades of the past century, but were so inconclusive that they require no discussion.[35] We owe our present knowledge of the chemical composition of this oil chiefly to the work of Wallach,[36] Semmler,[37] Thoms,[38] Power and Salway,[39] and Schimmel & Co.[40] These investigators have reported the presence of the following compounds (listed approximately according to their boiling points):

d- and *l*-α-Pinene. As far back as 1862 Schacht [41] observed in oil of mace a hydrocarbon which gave a solid hydrochloride; he named this hydrocarbon "Macene." Years later, Wallach identified "Macene" as α-pinene (nitrolbenzylamine m. 123°). It occurs in the lowest boiling fraction of the oil as an optically almost inactive mixture of *d*- and *l*-α-pinene.

Camphene. Identified by Power and Salway, who hydrated the terpene to isoborneol m. 207°–212° (phenylurethane m. 138°).

β-Pinene. Present only in small quantities. Characterized by oxidation to nopinic acid m. 126°–128° (Schimmel & Co.).

Dipentene. Identified by means of its tetrabromide m. 124°–125° (Wallach; Power and Salway; and Schimmel & Co.).

p-Cymene. Characterized by oxidation to *p*-hydroxyisopropylbenzoic acid m. 155°–156° (Schimmel & Co.).

d-Linaloöl. Oxidation to citral, the latter identified by preparation of the α-citryl-β-naphthocinchoninic acid m. 200° (Power and Salway).

1-Terpinen-4-ol. Identified in the fraction b. 205°–215° (Schimmel & Co.).

Borneol. Oxidizing the fraction b. 205°–215°, Power and Salway, among other products, obtained camphor (semicarbazone m. 238°); it was probably formed by oxidation of borneol originally present in the oil.

dl-α-Terpineol. The same authors also noted that the oil contains *dl*-α-terpineol, which they characterized by preparation of dipentene dihydroiodide m. 80°, and by oxidation to the ketolactone $C_{10}H_{16}O_3$, m. 62°–63°.

About eighty years ago Wright [42] expressed the opinion that the oil contains an alcohol b. 212°–218°, to which he referred as "Myristicol." In reality this alcohol is a mixture of 1-terpinen-4-ol, borneol, and α-terpineol.

Geraniol. Identified by means of its diphenylurethane m. 81°-82° (Power and Salway.)

Safrole. Characterized by oxidation to piperonal m. 34°–35° (Power and Salway).

[35] For a listing of these publications, see Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 598, footnote 1.
[36] *Liebigs Ann.* **227** (1885), 288; **252** (1889), 105.
[37] *Ber.* **23** (1890), 1803; **24** (1891), 3818.
[38] *Ber.* **36** (1903), 3446.
[39] *J. Chem. Soc.* **91** (1907), 2037. (These two authors used a "normal" and a "heavy" [i.e., rectified] oil in their investigations.)
[40] *Ber. Schimmel & Co.*, April (1910), 75.
[41] *Arch. Pharm.* **162** (1862), 106.
[42] *J. Chem. Soc.* **26** (1873), 549.

Digitized by Google Original from CORNELL UNIVERSITY

An Aldehyde(?). The substance in question had an odor reminiscent of citral and yielded a β-naphthocinchoninic acid compound m. 248°. Its identity, however, was not established (Power and Salway).

Myristicin. This phenolic ether $C_{11}H_{12}O_3$ occurs in the highest boiling fractions of nutmeg and mace oils. It is one of the most important constituents of the oils. The chemical constitution of myristicin was elucidated by Thoms.[43] (For details, see Vol. II of the present work, p. 531.) Myristicin is toxic and acts as a narcotic. When taken in sufficient quantities, it is liable to cause fatty degeneration of the liver.

The oil also contains several phenols, of which Power and Salway identified:

Eugenol. Benzoate m. 69°, diphenylurethane m. 107°–108°.

Isoeugenol. Benzoate m. 105°.

In the saponification lyes of the oil Power and Salway noted the presence of these acids:

Formic Acid. Identified as barium salt.

Acetic Acid. Identified as barium salt.

Butyric Acid. Identified as barium salt.

n-Caprylic Acid. Identified as silver salt.

A Monocarboxylic Acid $C_{12}H_{17}OCOOH$. Nonvolatile, insoluble in water; m. 84°–85°.

Myristic Acid. M. 54°; present in the oil free and esterified. Depending upon the length of distillation and the steam pressure applied, smaller or larger amounts of this acid and its esters occur in the oil. On evaporation of the oil, the acid remains in the residue. If large quantities are present, the acid may separate from the oil in crystalline form. In the early literature this crystalline deposit was called "Myristicin." It must not be confused with true myristicin, i.e., the phenolic ether $C_{11}H_{12}O_3$ described above.

As a result of their work, Power and Salway[44] reported the following quantitative composition for the nutmeg oil which they investigated:

d-Pinene, *d*-Camphene	About 80 per cent
Dipentene	About 8 per cent
d-Linaloöl, *d*-Borneol, *dl*-Terpineol, Geraniol	About 6 per cent
1-Terpinen-4-ol[45]	Small quantities
An Aldehyde with citral odor	Traces
Safrole	About 0.6 per cent

[43] *Ber.* **36** (1903), 3446.

[44] *J. Chem. Soc.* **91** (1907), 2037.

[45] This compound identified by Schimmel & Co. (see above) appears to be identical with the alcohol found by Power and Salway, which, on oxidation, yielded a diketone $C_8H_{14}O_2$, dioxime m. 140°.

Digitized by Google Original from CORNELL UNIVERSITY

(*Top*) A cardamom plant in Southern India. (*Bottom Left*) A ginger planting on the Cochin Coast (Southern India). A native holding a ginger plant, showing the rhizome. (*Bottom Right—Above*) A young pepper grove in Banka (Indonesia). The young shoots are supported by poles; (*Below*) bunches of pepper on the left, and pepper berries on the right side. Lampong (Indonesia). *Photos Fritzsche Brothers, Inc., New York.*

(*Top*) Production of sandalwood oil in Mysore State, India. Removal of the bark and sapwood from the heartwood of the sandal tree. *Photo Fritzsche Brothers, Inc., New York.* (*Right*) Shredding billets of sandalwood by power-driven rapidly rotating knives. *Photo Mysore Government Sandalwood Oil Factory, Mysore, India.* (*Bottom*) Production of sandalwood oil, West Australia. Sandalwood billets stacked up in front of a distillery. *Photo Plaimar, Ltd., Perth, West Australia.*

Digitized by Google
Original from CORNELL UNIVERSITY

Myristicin	About 4 per cent
Eugenol, Isoeugenol	About 0.2 per cent
Myristic Acid, free	About 0.3 per cent
Myristic Esters	Small quantities
Formic Esters, Acetic Esters, Butyric Esters, *n*-Caprylic Esters, Esters of Monocarboxylic Acid $C_{13}H_{18}O_3$	Small quantities

Power and Salway emphasized that these proportions are not absolute; in fact, they vary greatly with the quality and origin of the spice from which an oil is derived. The oil investigated by Power and Salway (d_{15} 0.869, α_D +38° 4′) was distilled from Ceylon nutmegs. Its relatively low specific gravity and elevated optical rotation permit the conclusion that the oil was particularly rich in terpenes. In other nutmeg oils the content of oxygenated compounds is probably much higher than in the oil examined by Power and Salway.

Use of Nutmeg and Mace Oils

Oil of nutmeg and the almost identical oil of mace are used widely for the flavoring of numerous food products, particularly baked goods, cakes, cookies, custards, puddings, pickles, etc. The oils find application also in table sauces, tomato catsup, and all kinds of savory preparations and dishes. If well blended, they lend a pleasant smoothness to flavor combinations.

As Power and Salway [46] found, oils of nutmeg and mace are somewhat poisonous, the toxicity being caused by the presence of myristicin (see above). In pharmaceutical preparations—the oil has been recommended for treatment of inflammations of the bladder and urinary tract [47]—large doses must be avoided.

Oil of nutmeg is used also in certain types of perfumes, and for the flavoring of dentifrices.

Oil of *Myristica Fragrans* Houtt., from the Leaves

Meyer [48] steam-distilled dried leaves of the true nutmeg tree *Myristica fragrans* Houtt., and obtained 1.56 per cent of a colorless volatile oil with these properties:

[46] *Am. J. Pharm.* **80** (1908), 563.
[47] Fühner, *Med. Welt* **30** (1940), 779. *Merck's Jahresber.* **55** (1943), 157.
[48] *Ing. Nederland-Indië* **8** (1941), No. 1, VII, 7. *Chem. Abstracts* **35** (1941), 4549.

Digitized by Google Original from CORNELL UNIVERSITY

Specific Gravity at 27.5°/4°	0.8772
Optical Rotation at 27°	−3° 30′
Refractive Index at 26°	1.4742

The oil contained 80 per cent of *α-pinene* and about 10 per cent of *myristicin.*

The oil is not produced on a commercial scale.

Oil of *Myristica Succedanea* Bl.

As was pointed out in the monograph on "Oil of Myristica," there are several species of *Myristica* other than *fragrans,* the kernels of which enter the spice trade as nutmegs. The botanical origin of these is not always easy to establish, but there are a few quite well-known species which will be described briefly here.

The most important species of these is probably *Myristica succedanea* Bl., locally called "Pala Maba," which originates chiefly from the island of Ternate in the Moluccas. According to Nijholt,[49] nutmegs and mace derived from *Myristica succedanea* Bl. are only slightly, if at all, inferior to first quality Banda nutmegs and mace. The kernels of the species *succedanea* are somewhat more elongated, and often smaller than those of the Banda type (which is true *Myristica fragrans* Houtt.). For this reason adulteration of the species *succedanea* with the inferior Papua nutmegs, which are also elongated and small, cannot easily be detected.

Van der Wielen and Hermans [50] distilled nutmegs of *Myristica succedanea* Bl. with superheated steam and reported these data:

	Kernel Oil
Yield of Oil	4.921%
Specific Gravity at 15°/4°	0.9227
Optical Rotation at 15°	+31° 14′
Refractive Index at 20°	1.4901

Oil of *Myristica Argentea* Warb.

The kernels derived from *Myristica argentea* Warb., a native of New Guinea, have for a long time been known in the spice trade as "New Guinea," "Papua," or "Long Nutmegs." Occasionally (but wrongly) they are also called "Macassar Nutmegs" because the nuts (which originate from New Guinea) are often shipped first to Macassar, from there entering international trade. The term "Long Nutmegs" arose from the fact that

[49] Private communication from Dr. J. A. Nijholt, Director of the Laboratorium voor Scheikundig Onderzoek, Buitenzorg, Java.

[50] *Festschrift für Alexander Tschirch,* Leipzig (1926), 328.

Digitized by Google Original from CORNELL UNIVERSITY

they possess a longer and narrower shape than the genuine nutmegs derived from *Myristica fragrans* Houtt. The "New Guinea" or "Papua Nutmegs" measure about 3 to 3.7 cm. in length, and about 1.5 to 2 cm. in width. They can easily be recognized by their elliptical shape and weak, rather poor odor and flavor. There are numerous varieties of false nutmegs, but commercially the varieties can be reduced to two, the difference being one of size: the larger ones are usually designated "Papua Nutmegs," the smaller ones "Macassar Nutmegs." Although known in the Far East and Europe for a long time, they have been imported to the United States only since World War II. However, they are unsuitable for distillation purposes, the yield and quality of the volatile oil being subnormal. The same holds true of the "Papua" and "Macassar" mace, which is also of inferior quality. On commercial distillation, "Papua Mace" yields only about 4 per cent of volatile oil.

Van der Wielen and Hermans [51] distilled nutmegs and mace of *Myristica argentea* Warb. with superheated steam and reported these data:

	Kernel Oil	*Mace Oil*
Yield of Oil	1.624%	6.956%
Specific Gravity at 15°/4°	0.9126	0.9272
Optical Rotation at 15°	+14° 52′	+26° 2′
Refractive Index at 20°	1.4848	1.4936

Oil of *Myristica Malabarica* Lam.

The dried seed of *Myristica malabarica* Lam., a native of India, is known in the trade as "Bombay Nutmegs," the mace as "Bombay," "False" or "Wild Mace." Like the "Papua Nutmegs," the "Bombay Nutmegs" are of elongated, elliptical shape (3 to 4 cm. long); hence the use of the latter as an adulterant of the former. The same is true of the corresponding mace, which has a dark red color, and narrow, long bands. Both "Bombay Nutmegs" and "Bombay Mace" are practically devoid of aroma, and so deficient in volatile oil that they cannot be used for distillation purposes.

[51] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

Digitized by Google

Original from
CORNELL UNIVERSITY

CHAPTER III

ESSENTIAL OILS OF THE PLANT FAMILY *ZINGIBERACEAE*

Digitized by Google

Original from
CORNELL UNIVERSITY

THE CARDAMOM OILS

Essence de Cardamome *Aceite Esencial Cardamomo*
Cardamomenöl *Oleum Cardamomi*

OIL OF *Elettaria Cardamomum* MATON VAR. *Minuscula* BURKHILL

Introduction.—The cardamom of commerce consists of the dried ripe fruit of *Elettaria cardamomum* Maton (fam. *Zingiberaceae*). There are two varieties of this species:

1. Var. *minuscula* Burkhill, also called *α-minor*. This, the smaller and more valuable of the two varieties, is cultivated chiefly in southern India (Malabar Coast and adjacent regions), and lately also in Ceylon; hence the trade name "Malabar," "Malabar-Ceylon," and "Mysore-Ceylon" cardamoms for this variety. Large quantities are used as spice and for extraction of the essential oil by distillation.

2. Var. *β-major* Thwaites, also called *Elettaria major*, or "Long Wild Cardamoms." This, the larger and less valuable of the two varieties, grows wild in Ceylon and is cultivated there on a much smaller scale than var. *minuscula*. Until about 1900 only the var. *β-major* was used for distillation of the essential oil, but since the beginning of the century the picture has changed completely, and now the var. *α-minor* has largely replaced the other as regards distillation.

Cardamom fruit is official in most pharmacopoeias. However, the United States and the British Pharmacopoeias confine the definition of cardamom to the decorticated seed only; moreover, the British Pharmacopoeia requires that the seed must have been *recently* removed from the capsules. This latter point is important, because cardamom seed removed from the shell loses a substantial amount of volatile oil by evaporation (about 30 per cent in eight months), whereas husk-protected seed loses only a comparatively small quantity (Clevenger [1]).

The commercial term cardamom has been applied also to the aromatic capsules (fruit) of other plants belonging to the family *Zingiberaceae* (particularly to those of the genus *Amomum*) which are cultivated in Indonesia, Siam, Indo-China, and southern China. These, however, are little known

[1] *J. Assocn. Official Agr. Chem.* **17** (1934), 285.

Digitized by Google Original from CORNELL UNIVERSITY

in Europe and America, being used mostly in the Far East. Among them are the "Round Siam," and the "Round Chinese Cardamoms." The present monograph will deal exclusively with the official cardamom, *Elettaria cardamomum* Maton var. *minuscula* Burkhill; other cardamom types will be treated in separate monographs.

According to a report of the Colonial Institute,[2] Amsterdam, the export figure for cardamoms from 1930 to 1940 averaged 1,600 metric tons per year. Of these 60 per cent were "round" cardamoms (*Amomum*), and 40 per cent true cardamoms (*Elettaria*). The Netherlands East Indies exported about 100 tons, Siam 450 tons, and Indo-China 400 tons of "round" cardamoms per year, while British India shipped about 500 tons and Ceylon 150 tons of true cardamoms per year.

History.—The use of cardamom as a highly esteemed spice, a masticatory and an aphrodisiac by the wealthier classes of India goes back to early times. It was known to the Greeks and Romans. The first definite record of cardamom as a spice from the Malabar Coast, written by a European, appears to be that of the Portuguese navigator Barbose,[3] who in 1514 explored the west coast of southern India for spices. About thirty years later, Valerius Cordus submitted cardamoms to distillation, thus isolating the essential oil for the first time.

Description, Habitat, and Range.—*Elettaria cardamomum* Maton is a large perennial herb with a tuberous horizontal rhizome, which grows from 8 to 20 erect perennial leafy stems, 8 to 12 ft. in height. The rhizome also thrusts out flowering stems up to 3 ft. in length, which tend to spread horizontally and produce numerous pretty flowers arranged in panicles. The fruit is an ovoid, three-celled capsule, containing numerous seeds covered by an aril. The inside of the fruit is soft, almost cotton-like, protecting the seeds. The latter contain most of the essential oil, the hard pericarps very little (about 0.2 per cent). On drying, the fruit loses approximately 75 per cent of its weight.

To thrive, the cardamom plant requires—more than anything else—elevation, moisture, and shade. The herb grows abundantly, both wild and under cultivation, in the mountainous districts of southern India, Ceylon, and other tropical countries, at altitudes ranging from 2,500 to 5,000 ft. above sea level. Sections with an average temperature of 22° C., and an average yearly rainfall of 120 in. are best suited for the cultivation of cardamom. Equally important is shade (the plant thrives in moist mountain jungles).

The soil should be rich, with a high content of humus; even swampy ground is suitable. Loamy soil, such as that used for pepper and betel

[2] *Koloniaal Instituut, Amsterdam. Mededeeling* No. 58 (1942), 79.
[3] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. I, 122.

Digitized by Google Original from CORNELL UNIVERSITY

plantings may be satisfactory; in fact, cardamom is often planted as a secondary crop with pepper. In South India many growers raise cardamom along with coffee. If, for instance, a swampy stretch runs through a coffee plantation, it is sometimes planted with cardamom.

Planting and Cultivating.—In the mountain forests of tropical countries where the plant occurs naturally, it springs up spontaneously after removal of underbrush. In sections where conditions are still primitive, the natives simply locate a spot in a moist shady mountain forest where some cardamom plants are growing wild. Shortly before the rainy season starts, the natives root out any surrounding brush and weeds that may be harmful to the cardamom plants, at the same time making sure that a certain amount of light, necessary to proper growth of the cardamom, is admitted. The seeds already present in the ground germinate. When the young plants appear precautions are taken for their protection and they are then left to themselves for a year. The plants commence to flower at the end of the second year, and bear fruit a year later. A good crop can be expected in the fourth year. The plants remain productive for quite a few years. If growing in too great abundance, they may have to be thinned out; if the opposite condition holds, others may have to be planted. Each year the clearings should be weeded, the weeds being left on the ground to rot and to act as manure.

In the forests of Coorg and western Mysore cardamom plantings are started in February or March. For the purpose, a part of the forest is simply cut down, but rows of trees 20 to 30 yards wide are left standing between the cardamom plantings, to act as shade trees. The first harvest can be gathered in the fifth year; after this the planting may remain productive for eight years, when it starts to decline and has to be renewed.

These, in general, are the old and primitive methods of planting cardamom; they have been greatly improved in the course of the last fifty years, particularly in Ceylon, and along the Malabar Coast. Cardamom is now propagated either by division of the rhizomes ("bulbs"), or by seed grown in seed beds and nurseries. Seeds, however, germinate very slowly, and four months may elapse before the young shoots appear. In Ceylon the soil is thoroughly cleaned prior to planting, and holes are dug 12 to 15 in. deep, 1.5 to 2 ft. wide, and 7 ft. apart in both directions. The rhizomes should not be planted too deep, lest they start to rot. At present cardamom in Ceylon is propagated largely by seedlings, after they have been in a nursery bed for about a year. To thrive, they require rich and moist soil, with a humus content and ample shading. The two principal harvests take place in February/March and in August/September; smaller quantities can be harvested throughout the year, at two-month intervals. One acre produces

Digitized by Google Original from CORNELL UNIVERSITY

from 150 to 300 lb. of cardamoms per year. After eight years a planting starts to decline; in the twelfth year it has to be renewed.

Harvest and Preparation of the Fruit.—In general, the capsules should be gathered from the fruit stems just before complete maturity, when still somewhat green but beginning to turn yellow. If left on the fruit stems to ripen, the capsules will split open and eject their seeds. In modern practice each fruit is carefully cut off with scissors, a portion of its pedicel being left attached to each capsular fruit. Formerly, it was customary to pull off whole racemes of fruit—a wasteful procedure, because not all fruits ripen at the same time.

As was mentioned above, the essential oil and the flavoring principles of cardamom reside almost exclusively in the seed borne within the capsules; nevertheless the spice trade attaches great (perhaps too great) value to the external appearance of the capsules themselves. These are prepared for the market by curing, which can be achieved in several ways. If possible the capsules are slowly dried on clean dry mats by exposure to the sun in dry weather. Great care has to be exercised, however, because overrapid or too long drying may cause the capsules to swell, burst, and lose part of their seeds. Sun-drying also bleaches the capsules to some extent. In wet weather the capsules are placed on trays in racks, in special curing houses, and exposed to gentle heat. Artificially dried cardamoms retain their original green color. Occasionally the capsules are sprinkled with water, then bleached in the sun; this may improve the color of the pericarp, but usually increases the number of split fruits. When sufficiently dried, the pieces of attached stalks (pedicels) are clipped or rubbed off the capsules, and removed by winnowing or by cleaning in machines. The capsules are finally graded into different sizes by means of sieves. Split fruits, broken shells, and loose seeds must be removed. The final product may have to be air-dried once more, before it is packed into cases for shipment.

Since white or pale-colored cardamoms are preferred by some spice dealers, several methods have been devised for improving the color of the sun-bleached product. One of these methods consists in imparting a light coating of starch to the dried fruit; another practice is to bleach the cardamoms by fuming with burning sulfur.

Still another method of bleaching, frequently practiced in India, consists of a quite elaborate process: [4]

The cardamom pods are dropped into a large earthenware jar filled with clean water and some fruit of the soapberry tree (*Sapindus saponaria* L.). The mass is stirred vigorously by hand for a few minutes, allowed to rest,

[4] The author is greatly obliged to Dr. Karl Landes, New York, for the description of this process.

Digitized by Google Original from CORNELL UNIVERSITY

and stirred again. The fruits are then removed from the jar, washed clean in another tub of fresh water, taken out and placed into wicker baskets. After all the water has been drained off, the fruits are spread out and sprinkled with clean water, at half-hour intervals, throughout the night. In the morning the fruits are spread on drying mats, exposed to the sun for 4 to 5 hr., taken inside of a hut, sprinkled again, and finally exposed to the afternoon sun for 4 to 5 hr. This produces a good grade of bleached cardamoms.

As a supplement to our general description of the growing, harvesting and curing of cardamom in India and Ceylon, we shall add some observations by A. H. Khan [5] on the collection and drying of the spice as carried out in Madras Presidency:

Cardamoms occur naturally in the evergreen forests of the western Ghats, in Madras Presidency, flourishing best in rich loamy soil from 2,000 to 4,000 ft. above sea level. A typical area of natural cardamoms is the Silent Valley in Palghat Division, where the cardamoms are of the Malabar variety. Most private plantations, however, are of the Mysore variety, this being the more favored type. The plants begin to yield a small crop in the third year, and full crops from the fourth year on, after natural expansion of the plants has taken place, and the gaps have been filled in by additional hand planting.

The collection, which should begin when the seeds in the fruits start to turn dark, lasts from August through October. If the harvest is delayed too long, the over-ripe capsules may split on drying.

In regular plantations the cardamoms are collected very carefully, only the ripe capsules being picked throughout the harvesting period. This method, however, is too expensive for the collection of the wild cardamoms, which are spread over extensive forest areas. In the Silent Valley, therefore, harvesting consists of pulling out whole panicles of fruits; each panicle should bear at least 75 per cent ripe fruits. This may appear wasteful, but under the conditions given there is no alternative. The coolies hand over their collection to the forester after removing the fruits from the rachis, but since their wages are based on a volume measure, they are likely to remove as much of the main stalk as possible. The subordinate in charge of collection, therefore, should see that nothing of the pedicel (the direct stalk of the fruit) is included for measurement. Although the green cardamoms from the Silent Valley can stand two days of rough storing plus an additional day in transit without any appreciable deterioration in quality, it is best to send them down immediately after collection to the drying sheds in the plains, about 10 miles distant. Here they are given an intense

[5] *The Indian Forester* (April 1944). Cf. *Flavours* 7, No. 6 (1944), 20.

Digitized by Google Original from CORNELL UNIVERSITY

cleaning, which consists of nipping the stalks from individual capsules, a job done very cheaply by women, girls, and boys.

The original sheds were thatched buildings with bamboo *thatti* walls 12 ft. high, made air-tight by plastering with mud. The portions of the walls abutting on the furnaces were of sheet zinc. The ceiling was constructed of unplastered bamboo mats to allow the vapor to escape. Each shed consisted of a drying room, two small side rooms for feeding the furnaces, and a veranda for the coolies engaged in cleaning the green cardamoms. The drying room was 15 × 30 ft., and consisted of two rooms—one above the other, and separated by a strong lattice-work partition 6 ft. above the floor. Two iron furnaces, 2 × 4 × 3 ft. each, were placed diagonally opposite each other in the corners of this room, 3 ft. away from the side walls. A smoke-tight zinc pipe, 9 in. in diameter, ran from each of these furnaces along each side wall, through the ends and vertically as an outside flue. Thus in the lower room, there were two parallel pipes 8 ft. apart and running the length of the room.

After removal of the stalks, the green cardamoms are spread evenly on the floor of the drying room and on mats on the middle partition, the capsules touching each other. About 1,250 lb. of green cardamoms can thus be spread at one time in a drying room of 15 × 30 ft. The furnaces are fed with thick green fuel (two cartloads being necessary to dry 1,250 lb. of cardamoms, yielding about 135 lb. of dried cardamoms), and the doors of the shed are closed. Care should be taken that there are no leaks in the pipes, as the smoke spoils the color of the spice. If the furnaces are fed constantly, it takes about 30 hr. for the green cardamoms to dry completely, those in the upper room drying about 4 to 6 hr. earlier than those below. The cardamoms near the furnaces on the floor, and those directly above them dry the fastest. It is essential that the cardamoms be removed from the drying room as soon as the drying is complete, as they lose their color if allowed to remain in the heat. Experience in the Silent Valley has proved

where they are first rubbed on a wide-meshed sieve and then winnowed, to separate the grainless, shriveled fruits and other rubbish. They are then packed immediately in good double gunny sacks and stored in a dark room, after weighing. They should never be left heaped-up in the storeroom as, in wet weather, they soon swell up, absorbing moisture, and becoming mildewed if packed in bags in this condition. The dried cardamoms should be stored in a dark room, as light spoils their color.

Loss can occur in two stages: first, when the stalks are removed from the capsules, and second, in the course of drying. The loss after removal of the stalks from the capsules should be about 25–30 per cent. A higher loss indicates that the collection is not being done properly in the hills. In the case of the Silent Valley cardamoms (Malabar variety), the weight is reduced from 25 lb. green to 2¾ lb. dried. The loss in the case of the Mysore variety is less, as the Malabar cardamoms are more juicy and exhibit wider variance with the locality of production. It is worth while, therefore, to determine the standard loss to be expected for a new locality by careful records at the very first consignment, as this affords a good check for later control in the depot.

Trade Varieties.—The dried fruit of *Elettaria cardamomum* Maton var. *minuscula* Burkhill is a three-angled, ovoid or oblong, three-celled capsule, about 1 to 2 cm. long, slightly rounded at the base, and shortly beaked at the apex. The color of the green or unbleached capsules ranges from gray to green-brown; that of the bleached capsules from cream to buff. Each cell contains two rows of seeds, which are mostly agglutinated into groups of 2 to 7 by the adhering membranous aril. The length of the individual seeds ranges from 3 to 4 mm., their color from pale orange to dark brown. They have an aromatic, pungent and slightly bitter taste, and an odor reminiscent of eucalyptus. The pericarps are tough, and possess very little odor and flavor.

Formerly the trade terms "lesser," "middle" and "larger" or "shorts," "short-longs" and "long-longs," respectively, were applied to cardamoms of various origin, the terms "larger" or "long-longs" including the large wild-growing cardamoms (*Elettaria cardamomum* Maton var. *β-major* Thwaites) from Ceylon. These terms are no longer employed in their old sense, and others have come into use. The official cardamoms (from *Elettaria cardamomum* Maton var. *minuscula* Burkhill) are now often classified as "shorts" and "short-longs." The former are usually broad and plump, the latter finer-ribbed, and lighter than the "shorts." The Malabar cardamoms are of highest value; they consist of both types. The Mysore cardamoms are considered of next best grade; they consist mostly of "shorts," but are less pungent in flavor than the Malabar. Both the Malabar and the Mysore cardamoms are now grown also on the island of Ceylon; hence the terms

Digitized by Google Original from CORNELL UNIVERSITY

"Malabar," "Malabar-Ceylon," and "Mysore-Ceylon" cardamoms. Aside from these, there are the Mangalore and the Alleppi cardamoms, grown near the port of Mangalore, and in Travancore and Cochin, respectively.

Some spice exporters in the ports of southern India evaluate cardamoms according to their origin:

1. Travancore State. Producing regions lie along the Malabar coast. The spice is shipped from the ports of Cochin and Alleppi; hence the designation "Alleppi Greens." Often the spice is first sent to Bombay and Madras, the headquarters of many Indian spice dealers, and exported from there. "Alleppi Greens" are the cardamoms most suitable for distillation. The best time to purchase the spice is right after the harvest, i.e., in October/November, when it is still relatively fresh and freely available.

2. Mysore State. Cardamoms grown here are also of very good quality; they resemble those from the neighboring province of Coorg.

3. Province of Coorg. This quality often consists of the second or third picking of the cardamom-bearing plant. The pods are not green, but usually yellow, and often split, thus exposing the seed to the air. Coorg cardamoms, although slightly inferior to those from the Malabar coast as regards appearance, are said to have a fair content of essential oil. Principal shipping ports of the "Coorg Greens" are Mangalore and Cochin; often the spice is sent to Bombay or Madras for export.

As regards exports from the island of Ceylon, a well-known exporter in Colombo ships cardamoms under these designations:

(1) Green Cardamoms:
  Kandy Type—relatively large, of dark greenish color.
  Copernicus Type—slightly smaller than the "Kandy"; color generally green, but some capsules have an off-color.
  Green Faq. Type—small cardamoms with a gray-green color.
(2) Bleached Cardamoms:
  Malabar Half-Bleached—fair average quality of the season; rather small capsules.
  Curtius—fair-sized, rather long capsules.
  Cleophas—fair-sized, roundish capsules.
(3) Seeds:
  Crispus Type—freshly removed seeds, obtained by the husking of either green or bleached capsules.

In general, the trade distinguishes between decorticated cardamoms, green cardamoms, and bleached cardamoms.

Digitized by Google
Original from CORNELL UNIVERSITY

Decorticated Cardamoms, viz., the seed removed by hand from the capsules, are supplied chiefly by Alleppi and Mangalore in India, and by Guatemala (C.A.). The seed is used mostly by the spice and bakery trade for the flavoring of sausages, pastry, and confectionery. Principal consumers are the Scandinavian countries. Some of the seed is employed for the flavoring of "Aquavit," a well-known Swedish liqueur.

Green Cardamoms are most suited for distillation. They are firm to the touch, and tightly closed, thereby protecting the aromatic, oil-containing seeds inside of the pods. Green cardamoms are shipped chiefly from Alleppi and Mangalore, and to a lesser extent from Ceylon.

Bleached Cardamoms are prepared by bleaching of the green fruits. They are classified according to size:

1. Bold
2. Medium Bold
3. Medium
4. Small

The bolder the cardamoms, the more expensive they are. In the United States bleached cardamoms are used mostly in pickling spices and in packaged goods.

Distillation.—As has been mentioned, perhaps too much importance is attached to the appearance and color of the capsules, particularly if they are to be used for distillation purposes. Since the odorous principles are contained almost exclusively in the seed, it would seem sufficient that the capsules enclosing the seed be firmly closed (not partially split), and that the spice itself be of recent harvest. Clevenger [6] proved that:

1. For all practical purposes the husks from cardamom fruits may be considered inert.[7]
2. Seed from green cardamoms yields on the average more volatile oil than seed from bleached cardamoms.
3. Cardamom seed, imported as such, yields on the average less volatile oil than that recently removed from the husks. This is undoubtedly due to the lack of protection by the husks.
4. The loss of volatile oil in husk-protected seed is comparatively small, even after eight months.
5. The loss of volatile oil in cardamom seed removed from the shells is

From the findings of Clevenger, and from the experience of commercial producers, it appears that the best material for distillation of cardamom oil is "green," "Malabar," or "Ceylon-Malabar" cardamoms of recent harvest. Fruit from Mysore or Coorg is also well suited for distillation. The capsules do not have to be bleached; in fact, bleached cardamoms are only a fancy grade in the spice trade. The most important factor is that the capsules be tightly closed, and not split, and that they contain as much seed as possible. External appearance of the spice plays no role in distillation. Prior to distillation, the fruits should be crushed and charged into the stills immediately afterward. They yield from 3.5 to 7.0 per cent of essential oil.

Note that no cardamom oil is produced in India and Ceylon; the spice is exported to Europe and America for use as such, or for distillation.

Cardamom Oil from Guatemala.—In 1945 Guatemala started to produce small quantities of cardamom oil from domestically grown seed. Since this new industry has grown substantially in the course of the last years, it may interest the reader to learn some details about its development, present status, and future possibilities.

According to Ippisch,[8] cardamom bulbs, for reproduction purposes, were first introduced into Guatemala in the early years of this century. They were imported from Ceylon or India, with the assistance of a New York broker, and planted in the northern part of Guatemala, in the area of Alta Verapaz (Cobán). The altitude here is about 2,000 ft., and rainfall exceeds 140 in. per annum.

Production of seed increased considerably after World War I, largely in the German estates located in the vicinity of Alta Verapaz. Decorticated seed material in tins was exported to Europe (Hamburg being chief port of entry). When the United States became engaged in World War II, the German estates were expropriated by the Guatemalan Government and all exports went to the United States. Production of the crop soon decreased, since the new managers, appointed by the government, lacked sufficient knowledge to grow it properly; however, tempted by the prevailing high prices, farmers in the neighborhood of the confiscated estates began

through local export companies, chiefly to the United States, and to a smaller extent to Belgium and Sweden.

The plantations are located at altitudes ranging from 2,000 to 4,000 ft., in areas where the soil is fairly moist, and retentive of water. Valleys sheltered from the wind are good locations for planting. Old coffee plantations, protected by the shade of leguminous trees, are frequently used. Common practice is to plant the bulbs at intervals of 8 by 8 ft., or even less (if possible, 6 by 6 ft.). The holes are about 15 in. deep and 2 ft. square. Several pounds of cattle manure are placed into each hole. The latter is then filled with good surface soil, the soil and manure being well mixed. The most common method of propagation is by division of the whole stool of a mature plant. At least two tubers are planted in each hole. Propagation by seed is never practiced. The soil around the plant must be cleaned two or three times a year, until the plant is sufficiently large to resist excessive weed growth. Stems which turn yellow or brown, or which have racemes growing from their bases, should be cut out. Any leaves, either from the cardamom itself or from the protecting shade trees, are removed from the hollow inside the stool, and earth is scraped up around the base of the stems to be placed over the tubers.

The best sign of a flourishing crop is the presence of a large number of healthy shoots, since each of these shoots produces a flowering raceme from its base. In fertile soil stools of mature plants may attain 5 ft. in diameter. The first crop is obtained in the second year after planting. A really fair crop, however, can be expected only in the third or fourth year. The harvest increases, from this time, until the eighth or ninth year, when it begins to decline.

The flowers on the racemes remain open for about a week; but three months elapse before the fruit matures. In Guatemala cardamoms ripen in December/January, and occasionally as late as February. In some years it is possible to harvest a secondary crop in March/April, before the beginning of the rainy season.

The green pods (capsules) containing the seeds are collected and carried by Indians to the farmsteads, where they are dried in airy concrete patios, similarly to coffee. When harvested at the proper time, the seeds are black; each pod contains up to 24 seeds. The most primitive way of separating the seed from the pods is by grinding them by hand on stones—a very ancient method used by the Mayans in treating corn. Nearly all Guatemalan seed is produced in this way, mechanical means (a specially adapted hammer mill and a special seed cleaner) being limited to two farms.

Production of small quantities of oil began in 1945, the amount representing an unimportant percentage of the crop. Two types of raw material are employed: (a) good seed, properly ground. The resulting fine powder

Digitized by Google Original from CORNELL UNIVERSITY

is distilled in thin layers. (b) Broken seed, powder and pods—i.e., waste material obtained in the separation of seed from the pods. The yield of oil from type (a) averages 6 per cent; that from type (b) ranges from 2.5 to 3 per cent.

The oil derived from the two types of material just described has not yet found full approval in the United States, perhaps because local methods of distillation are backward; or perhaps because green capsules chiefly are used for distillation in the United States. However, the Guatemalan oil has been accepted in Europe. Only limited quantities are exported.

Exports of decorticated seeds from Guatemala approximate 80,000 lb. annually, representing about one-third of the consumption in the United States. Compared with those from Ceylon and India, the exports from Guatemala are gradually increasing. This fact encourages efforts to enlarge production, both of the seed and the oil, and to improve material and equipment.

Physicochemical Properties of Cardamom Oil.—Oil of cardamom derived from the fruit or seed of *Elettaria cardamomum* Maton var. *minuscula* Burkhill is a colorless, or almost colorless liquid, with a spicy odor, reminiscent of eucalyptus.

Gildemeister and Hoffmann [9] reported these properties for the oil:

Specific Gravity at 15°	0.923 to 0.941
Optical Rotation	+24° 0′ to +41° 0′
Refractive Index at 20°	1.462 to 1.467
Acid Number	Up to 4.0
Ester Number	92 to 150
Solubility	Soluble in 2 to 5 vol. and more of 70% alcohol

Oils distilled under the author's supervision in Seillans (Var), France, from fruit imported from South India exhibited the following values:

Specific Gravity at 25°/25°	0.922 to 0.927
Optical Rotation	+22° 0′ to +25° 55′
Refractive Index at 20°	1.4640 to 1.4672
Acid Number	1.4 to 5.6
Ester Number	85.4 to 98.0
Solubility	Soluble in 2.5 to 3.5 vol. of 70% alcohol and more

Oils produced by Fritzsche Brothers, Inc., New York, from imported fruit, chiefly "Alleppi Greens," had properties varying within these limits:

Specific Gravity at 25°/25°	0.924 to 0.931
Optical Rotation	+22° 0′ to +27° 23′

[9] "Die Ätherischen Öle," 3d Ed., Vol. II, 445.

Digitized by Google Original from CORNELL UNIVERSITY

Refractive Index at 20°	1.4630 to 1.4672
Acid Number	1.4 to 5.6
Ester Number	88.2 to 121.8
Solubility	Soluble in 2.5 to 3.5 vol. and more of 70% alcohol

Two samples of cardamom oil produced in Guatemala, and examined in the laboratories of Fritzsche Brothers, Inc., New York, exhibited the following characteristics:

	I	*II*
Specific Gravity at 25°	0.931	0.924
Optical Rotation	+39° 14′	+30° 10′
Refractive Index at 20°	1.4640	1.4642
Acid Number	0.7	1.3
Ester Number	151.6	125.2
Saponification Number	152.3	126.5
Cineole Content	...	About 20%
Solubility	Soluble in 2 to 2.5 vol. and more of 70% alcohol	Soluble in 3 vol. of 70% alcohol; slightly opalescent in 10 vol.

The two oils had normal properties; their odor was very good. Other samples of Guatemala-distilled cardamom oil examined by the same firm had somewhat abnormal properties, the result, probably, of improper or careless distillation.

Distilling cardamoms (obtained from various crude drug firms) in a Clevenger apparatus, Fischer, Tornow and Proper [10] obtained oils with these properties:

Specific Gravity at 25°/25°	0.9213 to 0.9318
Optical Rotation at 25°	+21° 49′ to +33° 27′
Refractive Index at 20°	1.4624 to 1.4660
Acid Number	1.26 to 3.59
Ester Number	113.08 to 176.29

Clevenger [11] experimentally distilled cardamom seed separated from *bleached* fruit (I), cardamom seed separated from *green* fruit (II), cardamom seed imported from India (III), and cardamom seed imported from Guatemala (IV). The oils thus obtained had properties varying within the following limits:

[10] *Bull. Natl. Form. Comm.* **13**, No. 1–2 (1945), 7.
[11] *J. Assocn. Official Agr. Chem.* **17** (1934), 283.

Digitized by Google Original from CORNELL UNIVERSITY

	I	II	III	IV
Yield of Oil, in cc. per 100 g. of Seed	5.2 to 11.2	6.6 to 11.2	3.4 to 8.0	3.5 to 8.6
Specific Gravity at 20°/20°	0.922 to 0.938	0.923 to 0.930	0.923 to 0.932	0.923 to 0.932
Optical Rotation at 20°	+27° 0′ to +36° 42′	+20° 6′ to +32° 42′	+20° 42′ to +36° 42′	+27° 42′ to +36° 6′
Refractive Index at 20°	1.461 to 1.467	1.461 to 1.464	1.461 to 1.467	1.463 to 1.467
Acid Number	1.8 to 4.8	1.1 to 3.4	1.0 to 4.5	0.8 to 5.6

Other data reported by Clevenger show that the physicochemical characteristics of the volatile oils obtained from the capsules (fruit) including the seed, and from the seed alone, are practically identical.

In his work on cardamom oil, Clevenger [12] also found that the time required for complete saponification of the oil approximates 3 hr. The reason for this prolonged period of saponification is the presence of substantial quantities of terpinyl acetate in the oil.

Chemical Composition.—Although oil of cardamom derived from *Elettaria cardamomum* Maton var. *minuscula* Burkhill has been a very important spice oil for a long time, relatively little is known about its chemical composition. More than a century ago, Dumas and Péligot [13] observed the presence of crystals of terpin hydrate in an old Malabar cardamom oil; this compound probably originated from terpineol, a substance identified in the oil more than fifty years later. The oil has been investigated by Schimmel & Co.,[14] Parry,[15] Wallach [16] and Moudgill,[17] who reported the presence of the following compounds in the oil:

Limonene. Noted by Parry.

Sabinene(?). Presence possible (Moudgill).

Cineole. Identified by Schimmel & Co., who prepared the iodol compound m. 112°–113°.

d-α-Terpineol. Isolated from the fraction b_{14} 150°–164° of the saponified oil by Schimmel & Co., who identified the terpineol, m. 35°–37°, α_D +81° 37′ (in the superfused state), by means of the phenylurethane m. 112°–113°, $[\alpha]_D^{20}$ +33° 58′ (in 10 per cent alcoholic solution), and by preparation of the nitrosochloride. The latter was converted to a nitrolpiperidine m. 151°–152°, which melting point was 8° lower than that of the optically inactive terpineol nitrolpiperidine.

Terpinyl Acetate. Schimmel & Co., and Wallach found that the *d*-α-terpineol occurs in the oil in large part as acetate.

Borneol. Reported as a constituent of the oil by Moudgill; m. 198°

An Acid(?). The same author also noted that the oil contains an acid with an odor reminiscent of cuminaldehyde. Its molecular weight was determined as 182(?).

Use.—Like the spice itself, the essential oil is employed widely for the flavoring of various food products, such as cakes, confectionery, gingerbread, sausages, and pickles. It finds use also in spicy table sauces, curry preparations, and in certain bitters and liqueurs.

Medicinally, the oil is frequently employed as an adjuvant or corrective of tonic, carminative, and purgative preparations.

Suggested Additional Literature

Arno Viehoever and Le Kya Sung, "Common and Oriental Cardamoms," *J. Am. Pharm. Assocn.* **26** (1937), 872.

Oil of *Elettaria Cardamomum* Maton Var. *β-Major* Thwaites

The so-called "Long Wild Cardamoms," also known as *Cardamomum majus* or *Cardamomum longum,* are derived from *Elettaria cardamomum* Maton var. *β-major* Thwaites, and originate on the island of Ceylon; hence the popular name "Ceylon Cardamoms," or "Long Ceylon Cardamoms." The plant grows wild in the forests in the interior of Ceylon. It is also cultivated on a small scale near Kandy, the capital of the island. The dried fruit consists of a lanceolate-oblong, triangular capsule, up to 40 mm. long and 6 to 8 mm. broad, grayish-brown or dark brown in color. The fruit offered on the market frequently retains the long, cylindrical, three-lobed calyx at one end, and at the other end the fruiting stalk. The seeds are angular, yellowish-red, and possess the characteristic odor and flavor of cardamom.

Until about 1900 almost all oil of cardamom was distilled from this variety; since then, however, the var. *minuscula* Burkhill has been used for this purpose (see the preceding monograph). Nevertheless, a brief description of the oil derived from the var. *β-major* Thwaites is included here.

According to Gildemeister and Hoffmann,[18] distillation of the dried crushed fruits yields from 4 to 6 per cent of volatile oil.

Physicochemical Properties.—The oil distilled from long Ceylon carda-

Saponification Number.....	25 to 70
Solubility.....	Turbid in 70% alcohol. Soluble in 1 to 2 vol. and more of 80% alcohol

An oil derived from *Elettaria cardamomum* var. *β-major* and analyzed by Sage[20] exhibited the following values:

Specific Gravity at 15.5°.....	0.909
Optical Rotation at 20°.....	+16° 30′
Refractive Index at 25°.....	1.474
Acid Number.....	1.1
Ester Number.....	12
Solubility.....	Soluble in 1 to 2.5 vol. of 70% alcohol

Compared with cardamom oil from the var. *minuscula* Burkhill, the oil derived from the var. *β-major* Thwaites has a considerably lower specific gravity and optical rotation. It is particularly by the difference in their optical rotations that the two oils can be distinguished.

Chemical Composition.—The oil has been investigated by Weber,[21] and by Wallach,[22] who reported the presence of these compounds:

Sabinene. In the fraction b. 165°–167°; identified by oxidation to sabinenic acid m. 56°–57° (Wallach).

Terpinene. Passing gaseous hydrogen chloride through the fraction b. 170°–178°, Weber obtained terpinene dihydrochloride m. 52°. The fraction b. 178°–182° yielded terpinene nitrosite m. 155°. (Terpinene as a new terpene was first reported by Weber.)

1-Terpinen-4-ol. Investigating the fraction b. 205°–220°, Weber believed he had identified α-terpineol as a constituent of the oil. Later, however, Wallach proved that the terpene alcohol described by Weber was not α-terpineol, but the isomeric 1-terpinen-4-ol (cf. Vol. II of the present work, p. 198). Wallach identified this compound by means of its dihydrobromide m. 59°, and by oxidation to *p*-menthane-1,2,4-triol, m. 128°–129°.

1-Terpinen-4-yl Formate and Acetate. The oil contains formates and acetates of 1-terpinen-4-ol. Calculated on the basis of the ester number, the ester content of the oil ranges from 8 to 24 per cent.

A Solid Compound(?). Separated from the distillation residue. It melted at 60°–61°, after recrystallization from alcohol.

Use.—The small quantities of oil distilled from long Ceylon cardamoms have the same use as the oil derived from the var. *minuscula* Burkhill (see the preceding monograph).

Oil of *Amomum Cardamomum* L.

As was mentioned in the introduction to the monograph on "Oil of Cardamom," there are other members belonging to the fam. *Zingiberaceae* (and particularly the genus *Amomum*), the fruits of which resemble those of *Elettaria cardamomum* Maton, the true cardamom. One of them is *Amomum cardamomum* L., the so-called "Siam," "Round" or "Cluster Cardamom," which grows in Siam, Java, Sumatra, and other parts of the East Indian Archipelago. The fruits are now seldom encountered in Europe and America. At one time the fruit was official in the French Codex.

Round or Siam cardamoms occur in small compact bunches; they are smaller than a cherry, roundish, somewhat ovate, and possess a strong camphoraceous and aromatic flavor, resembling that of true cardamoms. (*Elettaria cardamomum* Maton).

Distilling the seed of *Amomum cardamomum* L., Schimmel & Co.[23] obtained 2.4 per cent of a semisolid liquid m. 42°, with an odor reminiscent of camphor and borneol. The oil had these properties:

Specific Gravity at 42°	0.905
Optical Rotation at 42°	+38° 4′
Saponification Number	18.8
Saponification Number after Acetylation	77.2
Alcohol Content, Calculated as Borneol	22.5%
Solubility	Soluble in 1.2 vol. of 80% alcohol

Another oil of *Amomum cardamomum* L., investigated in Buitenzorg[24] (Java), had the following properties:

Specific Gravity at 26°	0.909
Optical Rotation	−0° 20′
Acid Number	0.8
Saponification Number	14
Cineole Content (Resorcinol Method)	12%

In the oil which they had distilled from the seed of *Amomum cardamomum* L., Schimmel & Co.[25] identified *d-borneol* and *d-camphor*. The crystalline mass separating from the oil consisted of approximately equal parts of *d*-borneol and *d*-camphor.

Oil of *Amomum cardamomum* L. is not produced on a commercial scale.

[23] *Ber. Schimmel & Co.*, October (1897), 9.
[24] *Jaarb. Dep. Landb. in. Ned.-Indië*, Batavia (1911), 48.
[25] *Ber. Schimmel & Co.*, October (1897), 9.

Digitized by Google Original from CORNELL UNIVERSITY

Oil of *Amomum Globosum* Lour.

Another of the unofficial cardamoms is the "Large Round Chinese Cardamom," derived from *Amomum globosum* Lour., an evergreen said to resemble members of the genus *Myristica* in appearance. The plant is indigenous to southern China and now grows wild and under cultivation in the province of Kwangtung. The fruits are round or globular, pale yellow, with an average diameter and thickness of 15 mm., longitudinally streaked, tapering at both ends, these latter covered with numerous long nonglandular hairs. Each fruit contains about 24 seeds, possessing a pleasant aromatic odor and flavor, similar to that of true cardamom (*Elettaria cardamomum* Maton), but more camphoraceous. Viehoever and Sung [26] suggested that the fruit of *Amomum globosum* Lour. might be used as a substitute for the fruit of the official Malabar cardamom.

According to the same authors,[27] the seed of the large round Chinese cardamoms yields from 4 to 6 per cent of a volatile oil with these properties:

Specific Gravity	0.965 to 0.975
Refractive Index	1.462
Acid Number	1.5 to 3
Saponification Number	25 to 35
Solubility	Soluble in 4 to 5 vol. of 80% alcohol
Congealing Point	Does not congeal at −5°
Odor	Distinctly aromatic
Taste	Camphoraceous and cooling

Years earlier, Schimmel & Co.[28] had distilled "wild" cardamoms from Indo-China, reported to have been derived from *Amomum globosum* Lour. The oil (yield 4 per cent) had the following properties:

Specific Gravity at 15°	0.9455
Optical Rotation	+43° 54′
Refractive Index at 20°	1.47141
Acid Number	0.8
Ester Number	128.4
Solubility	Not soluble in 70% alcohol; soluble in 1 and more vol. of 80% alcohol

The values resembled those of true cardamom oil (from *Elettaria cardamomum* Maton), but the odor was quite different, recalling camphor oil, rather than true cardamom oil.

Oil of *Amomum Aromaticum* Roxb.

The fruits of *Amomum aromaticum* Roxb., also known as "Bengal Cardamoms" or "Winged Bengal Cardamoms" contain an essential oil with a strongly camphoraceous and cineole-like odor and taste.

Steam-distilling the fruit, Schimmel & Co.[29] years ago obtained 1.12 per cent of a volatile oil with these properties:

Specific Gravity at 15°	0.920
Optical Rotation	−12° 41′
Solubility	Clearly soluble in 1 and more vol. of 80% alcohol

The oil contained *cineole,* identified by the preparation of several derivatives.

The odor of the oil differed markedly from that of true cardamom oil (from *Elettaria cardamomum* Maton). The oil offers no practical interest.

Oils of *Aframomum Angustifolium* (Sonn.) K. Schum. and *Amomum Korarima* Pereira

There is much confusion in literature[30] regarding the taxonomy and nomenclature of the plant or plants from which the so-called "Madagascar" and "Cameroon Cardamoms" are derived. It is probably the fruit of *Aframomum angustifolium* (Sonn.) K. Schum., syn. *Amomum angustifolium* Sonnerat. (Formerly the fruit was known as *Cardamomum majus* Geiger.) Other species may also be involved. The plants occur in West Africa, East Africa, on the Seychelles Islands, and in Madagascar. The seeds possess an aromatic odor and flavor, slightly resembling that of true cardamom seed, but much more cineole- and cajuput-like.

Several oils have been described in literature:

I. An oil distilled by Schimmel & Co.[31] from East African seed (yield 4.5 per cent).

II. An oil distilled by the same firm[32] from Cameroon cardamoms (yield 2.33 per cent).

III. An oil distilled by Haensel[33] from the fruits of *Amomum korarima* Pereira (the *Cardamomum majus* fruit of Geiger), yield 1.72 per cent.

[29] *Ber. Schimmel & Co.,* April (1897), 48.
[30] Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 451.
[31] *Ber. Schimmel & Co.* April (1912), 132.

IV. An oil distilled from the same type of material as III (yield 1.2 per cent), and described by Holmes.[84]

These oils had the following properties:

	I	*II*	*III*	*IV*
Specific Gravity at 15°	0.9017	0.907	0.903	0.9038
Optical Rotation	−16° 50′	−20° 34′	−6° 49′	−3° 0′
Refractive Index at 20°	1.46911	...	...	...
Acid Number	0.4	...	...	3.6
Ester Number	4.2	...	...	22.1
Saponification Number	...	...	50	...
Saponification Number after Acetylation	...	...	107	...

Oils of this type are not produced on a commercial scale, chiefly because their odor is not sufficiently interesting and distinctive.

Oil of *Aframomum Melegueta* (Roscoe) K. Schum.

Aframomum melegueta (Roscoe) K. Schum. (syn. *Amomum melegueta* Roscoe) is a herbaceous perennial, native to Africa; it was introduced also to the West Indies, probably during the days of the slave trade. The plant occurs on the west coast of Africa from the Congo to the Sierra Leone; hence the name "Pepper Coast" or "Melegueta Coast" for this section of Africa. The shrub furnishes the "Grains of Paradise," "Grana Paradisi," in the trade also referred to as "Guinea Grains," "Melegueta" or "Mallaguetta Pepper." The name probably originates from the old empire of Melle in the upper Niger region, where countless slaves were captured and brought down the river to be sold on the coast.

"Grains of Paradise" in many aspects resemble the seeds of official cardamom. When rubbed between the fingers they give off a faint aromatic odor; their taste is hot and peppery. African natives have always esteemed these grains as a most wholesome spice; in fact, newly captured Negroes were so dependent upon the spice that slaving ships had to carry ample supplies on board. In Europe and America "Grains of Paradise" are now

Specific Gravity at 15°	0.8970
Optical Rotation	−3° 10′
Refractive Index at 20°	1.49116
Acid Number	2.7
Ester Number	41.2
Ester Number after Acetylation	63.9
Solubility	Not soluble in 90% alcohol. Soluble in 1 vol. of 95% alcohol, slightly turbid with more

When treated with a 3 per cent solution of sodium hydroxide, about 16 per cent of the oil went into solution.

Nothing is known about the chemical composition of the oil. The oil is not produced on a commercial scale.

Oil of *Zingiber Nigrum* Gaertn.

The so-called "Bitter-Seeded Cardamoms" are believed to be derived from *Zingiber nigrum* Gaertn., a plant growing in moist soil in the shady forests of the Far East, particularly in the province of Kwangtung (southeastern China). It is perhaps identical with *Alpinia allughas* Roscoe, a Cochin-Chinese species, about which there is still some controversy.[86] This evergreen herbaceous perennial is said to resemble *Amomum melegueta* (Roscoe) K. Schum. ("Grains of Paradise"), in having a long, slender, branched rhizome and an erect stem. The fruits are oval or ovate-oblong, dusky brown, pointed at both ends, and contain 25 to 30 seeds 3.5 mm. in length and 2 mm. in diameter.

Steam-distilling bitter-seeded cardamoms, Viehoever and Sung[87] obtained from 2 to 3 per cent of a volatile oil with these properties:

Specific Gravity at 40°	0.985
Refractive Index at 30°	1.471
Acid Number	7.50
Ester Number	79.53
Solubility	Soluble in 5 vol. of 80% alcohol

Investigating the oil derived from the fruit of *Zingiber nigrum* Gaertn., Karyione and Matsushima[88] isolated a terpene $C_{10}H_{16}$, b. 173°–176°, d_4^{23} 0.8564, $[\alpha]_D^{22} + 1° 16'$, and a sesquiterpene $C_{15}H_{24}$, b_{13} 139°–142°, d_4^{24} 0.9233,

[86] Cf. Viehoever and Sung, "Common and Oriental Cardamoms," *J. Am. Pharm. Assocn.* **26** (1937), 875, 877, 884.

[87] *Ibid.*

[88] *J. Pharm. Soc. Japan* (1927), 96. *Chem. Zentr.* (1927), II, 2405.

Digitized by Google Original from CORNELL UNIVERSITY

$[\alpha]_D^{30} + 16° 21'$. The oil apparently contained also a sesquiterpene alcohol which, however, was not examined.

The oil derived from bitter-seeded cardamoms has a camphoraceous and bitter taste. It is not produced on a commercial scale.

OIL OF GINGER

Essence de Gingembre *Aceite Esencial Jengibre* *Ingweröl*
Oleum Zingiberis

Description, Origin, and History.—Ginger, one of the most important and oldest of spices, consists of the prepared and sun-dried rhizomes of *Zingiber officinale* Roscoe (fam. *Zingiberaceae*). The rhizomes, known in the trade as "hands" or "races," reach the spice trade either with the outer cortical layers intact ("coated," or "unscraped ginger"), or with the outer coating partially or completely removed ("uncoated" or "scraped ginger"). To improve their appearance, some grades of ginger are bleached by various means, e.g., by liming.

Ginger possesses a warm pungent taste and a pleasant odor, hence its wide use as a flavorant in numerous food preparations and beverages, savory dishes, curries, baked goods, confectionery, gingerbread, soups, pickles, and many popular soft drinks. Like most pungent spices, ginger is consumed all over the world, particularly in tropical or warm countries. It dilates the superficial vesicles of the skin, resulting first in a feeling of warmth, then in increased activity of the sweat glands and perspiration, and finally in a marked cooling effect on the skin.

The odor of the rhizomes is caused by the presence of a volatile oil (1 to 3 per cent), which can be isolated by steam distillation of the comminuted spice. The pungent principles, on the other hand, are nonvolatile and must be extracted by percolation with suitable solvents, which procedure yields the so-called oleoresin of ginger (see below). Since the essential oil is

known to, and highly esteemed by, the ancient Greeks and Romans who obtained the spice from Arabian traders via the Red Sea. It was introduced to Germany and France in the ninth century, and to England in the tenth century. The Spaniards brought ginger to the West Indies and to Mexico soon after the conquest, and as early as 1547 the spice was exported from Jamaica to Spain. Since the rhizomes can easily be transported in a living state for considerable distances, the plant has been introduced to many tropical and subtropical countries and is now cultivated in several parts of the world, the most important producing regions being Jamaica (B.W.I.), Cochin and Calicut (Malabar Coast, South India), Sierra Leone and Nigeria (West Africa), southern China, and Japan. Of these, Jamaica produces what most connoisseurs consider the finest grade, possessing the most delicate aroma and flavor. The Cochin quality ranks perhaps second. It exhibits a characteristic lemon-like by-note, for which reason some experts prefer the Cochin ginger even to that from Jamaica. As a matter of fact, Cochin ginger often brings a somewhat higher price on the world market than the Jamaica quality. West African ginger is usually considered to rank third. Lately, however, the appearance of the West African spice seems to have improved. Nevertheless, compared with Jamaica and Cochin ginger, the West African exhibits a slightly camphoraceous, somewhat coarser odor and flavor, and darker color. Of all ginger grades, it possesses the greatest pungency and gives the highest yield of essential oil—hence its present wide use for the extraction of oleoresin and for the distillation of oil. Moreover, the African ginger is usually lower

rhizome, and an annual stem which rises 2 to 3 ft. in height. The plant does not exist in many forms or varieties, because it is usually propagated from cuttings (i.e., by asexual reproduction), and only very seldom, if at all, by seed.

According to Ridley,[2] ginger requires a tropical or subtropical climate, where the temperature is high for at least part of the year. Bright sunshine, as well as heavy rains, are necessary. In Jamaica, e.g., the annual rainfall averages 88 in.

The most suitable soil consists of a light, free, sandy loam. Stiff clays or coarse sands are not conducive to the cultivation of ginger. Sandy soils are apt to pack after a heavy rain and to become too dense for the rhizomes to develop. Wet swampy ground does not suit the plant at all, and areas liable to floods should be avoided. If the ground becomes too dry during the dry season, a system of irrigation will be needed. Swampy terrain may be utilized by systematic and careful drainage. The ideal ground for ginger is good garden soil, rich in humus, light and well worked, friable and fairly dry.

As regards elevation, in India the plant is grown successfully both in the low country and up to an altitude of 4,000 to 5,000 ft.

Prior to planting, the soil must be broken up finely with a hoe or plow, and if possible harrowed afterward. Ginger is always grown from cuttings of the rhizome. The points of the rhizome each contain a bud ("eye"), from which the plant grows. Frequently a portion of the crop is retained for planting stock. The cuttings should be from 1 to 2 in. long. Robles, Cernuda, and Loustalot[3] found that storage of planting stock of ginger

mulch effectively checked soil erosion. Alemar [6] also tested well decomposed sugar cane filter press cake, or cachaza, and well decomposed leaves of various tree species as mulches for the growing of ginger on clay loam soil containing a considerable amount of sand. He reported a doubling in the yield of rhizomes. Robles [7] found that the use of manure favored the yield of green ginger. Robles, Cernuda and Loustalot [8] noted that the application of composted manures resulted in significant increases in yields of fresh ginger. Moreover, higher yields of fresh and dry ginger were produced under shade. The results of these experiments indicate that ginger should be grown under partial shade to obtain the best yields of both fresh and dry ginger. The yield of ginger seven months after planting was double that harvested four months after planting.

Under favorable conditions the ginger plant appears aboveground about ten to fifteen days after planting, but as much as two months may be required before it begins to show. In Jamaica, planted ginger can be dug in December or January, or until March, whereas ratoon ginger is lifted between March and December. (The planters in Jamaica distinguish between "plantation ginger" and "ratoon ginger." Planted ginger gives the best results, and indeed represents the best method of cultivation. When the stock is left in the ground to throw up fresh stems, and produce fresh rhizomes, it is known as "ratoon ginger"—Ridley.)

The rhizomes can be lifted from the ground (harvested) when the green leafy stems turn yellow and wither; this usually happens after the flowering period. (However, the plant does not always produce flowers; indeed

The dried rhizomes contain a brownish cork beneath the epidermis, and a resinous, almost horny cortical layer. The parenchyma inside consists of a whitish mass, the cells being filled with starch. Minute sacs or glands containing essential oil and resin are scattered throughout the rhizomes, but are particularly numerous in the epidermal tissue. The dried rhizomes should be firm and full, free from any trace of mildew. They are rather brittle and crack easily; the presence of broken pieces lowers the value of a lot.

Commercial grades are known as "scraped" ("decorticated" or "uncoated"), and "coated ginger." Great care has to be exercised in the peeling operation because the essential oil and resin-bearing cells are located chiefly in the epidermal tissue. Excessive scraping depreciates the quality of the spice substantially. Scraped ginger is a grade from which the cortex has been removed partly or entirely. This is always the case with Jamaica ginger, and often with Cochin ginger. In "coated ginger," on the other hand, a good portion or all of the outer layer remains attached to the dried rhizome. African ginger is usually "coated," Calicut and Cochin ginger occasionally. In addition, there are bleached and unbleached gingers, the bleaching being accomplished by covering the rhizomes with a coat of lime or chalk. Liming has the effect of improving color and appearance, and of protecting the spice from mildew and attacks of weevils and other pests. In some producing regions the freshly dug rhizomes are parboiled (scalded) in water for 10 to 15 min. in order to destroy their vitality. The cleaned rhizomes ("hands" or "races") are then dried in the sun, without peeling.

water, and the more used, the whiter the ginger becomes (Ridley). The carefully washed "hands" are dried in the sun; this is usually done on barbecues, such as serve for the drying of coffee. Small producers use a framework of sticks, with boards, or palm or banana leaves, laid upon it; or a few large banana or palm leaves may be placed upon the ground and the ginger spread on them. The rhizomes are put out early in the morning, turned over at noon, and taken indoors in the evening. Unless proper care is exercised, they are apt to turn moldy in rainy or cloudy weather. Thorough drying requires six to eight days. In general, drying of ginger presents a delicate and difficult problem; in a very moist climate or during long spells of rain planters may lose their crops. Efforts have therefore been made to supplement sun-drying with artificial drying, and to dry the rhizomes without previous removal of the coat, which would save a considerable amount of labor. However, these experiments have resulted in rhizomes of a dark color and a flavor inferior to those of the sun-dried spice. Since Jamaica ginger is known and highly esteemed for its light color and fine flavor, these experiments must be regarded as unsuccessful. Nevertheless, further work along these lines, and with modern fruit-drying equipment, appears advisable.

On drying, fully developed rhizomes lose almost 70 per cent of their weight (about 40 per cent of this loss consists of surface moisture). The moisture content of dried ginger should not exceed 10 per cent, but is occasionally as high as 25 per cent in poor grades.

Production of Ginger in Jamaica.—In Jamaica (B.W.I.) ginger is grown at altitudes ranging from 2,500 to 3,500 ft., centers of production lying

pounds. Because of the danger of worm infestation, growers and dealers do not store the spice longer than three to four months. On the other hand, high temperatures in summer threaten loss of weight by excessive evaporation. Hence exporters try to prevent overstocking and usually export the entire yearly production.

Production of Ginger on the Malabar Coast.—There are two types of ginger produced on India's Malabar Coast, viz., the Calicut and the Cochin ginger. Both are characterized by their lemon-like odor and flavor, the Calicut spice being even more "lemony" than the Cochin product. Some experts consider ginger from the Malabar Coast the finest in the world. Manufacturers of ginger ale, particularly in Great Britain, use large quantities of this type, because it imparts not only pungency, but also an agreeable lemon-like flavor to beverages.

Calicut ginger is very bold, less fibrous, and more starchy than No. 1 bold Jamaica ginger, and usually well dried, and of creamy color when scraped.

Cochin ginger reaches the market bleached or unbleached; when bleached and scraped, it resembles the Jamaica spice, except for its lemon-like top note. The smaller pieces are simply sun-dried, without peeling.

According to Sennhauser,[11] on the Malabar Coast the freshly unearthed rhizomes are scraped by means of short, sharp knives, and dried in the sun for about four days. (Actual peeling has never been practiced in India.) The rhizomes so prepared enter the market as unbleached ginger. Exporters dry the spice for another two days and subsequently assort it; this process, called "garbling," consists of removing pieces that are too light, or the skin of which has not been removed properly. All ginger is then

Cochin Ginger, rough, washed and unassorted.
Cochin Ginger, bleached, unassorted.
Calicut Ginger, rough, washed, and unassorted.
Calicut Ginger, rough, bleached and unassorted.

Prior to World War II ginger was exported from India, chiefly to Germany and Scandinavian countries as grades A, B, C, D, and T. Grades A to C inclusive, were so-called "scraped" ginger, the grading being done according to size. Grade C thus consisted of very small pieces. Some of the thin parts of the rhizomes were cut off entirely during the scraping process; they were called "nibs" and sold as "Calicut Ginger D." The scrapings themselves entered the trade as "Calicut Ginger T." Calicut ginger A, B and C, after being bleached with sulfur fumes, were washed and bleached with lime; grades D and T were not limed. Since scraping was never practiced on the lower Malabar Coast, the Cochin D ginger did not consist of actual cuttings from larger pieces, but simply of small pieces of unscraped, unassorted and washed Cochin ginger. An average lot of ginger yielded from 50 to 60 per cent of A, B and C grades, about 43 per cent of D, and 7 per cent of T grade.

The following quantities of ginger, in tons, have been exported by steamer and rail (1934 to 1948 inclusive):

	Cochin	*Calicut*
1934.....	3,900	1,250
1935.....	1,400	600
1936.....	1,750	450
1937.....	3,200	275
1938.....	4,200	900
1939.....	5,500	1,000
1940.....	3,200	1,000
1941.....	3,900	1,600
1942.....	4,900	1,600
1943.....	...	...
1944.....	...	...
1945.....	...	...
1946.....	3,443	...
1947.....	4,122	873
1948.....	3,434	...

Production of Ginger in West Africa.—There are two principal qualities of West African ginger, viz., the better grade which originates from Sierra Leone, and the lower quality coming from Nigeria.

Annual production in Sierra Leone now averages 4.5 million pounds; at

ably the largest quantity the export market can absorb. A large part, up to 75 per cent, of the present production goes to the United States. Over 3,000 acres are now devoted to the production of ginger, areas of cultivation being centered in the southern provinces along the railway line, to facilitate transportation.

As regards Nigerian ginger, the crop is small, only about 250,000 lb. having been exported in 1947 and in 1948. In Nigeria ginger is grown on small, scattered holdings. The crop is marketed from January to February in only two market places in the entire country; both are located in Zaria Province, the towns being Katchia and Zonkwa. The markets are opened only twice, usually for a period of from seven to ten days.[12]

African ginger has a very pungent flavor; its odor is slightly camphoraceous, somewhat coarser than that of the Jamaica or Cochin spice. The rhizomes usually contain the skin (coated quality); or the cork may be partly removed on the flattened sides, leaving light brownish areas. The portions containing cork are longitudinally or reticulately wrinkled, and grayish brown. Internally, the color ranges from light yellow to brown.

According to Landes,[13] ginger from the Sierra Leone can easily be recognized by its dark color and unbleached condition. It is smaller than the third grade of Jamaica ginger, and usually much darker than even the Jamaica "ratoon ginger." Prices of the Sierra Leone ginger have for a long time been about 10 or 15 per cent lower than those of the Jamaica product, but lately this situation has changed somewhat because of the large demand for the Sierra Leone spice. The latter is popular for distillation purposes, for preparation of oleoresins, and for flavoring of cattle feed.

Nigerian ginger, although of fairly good quality, is somewhat too fibrous

to distribute the mass evenly on several trays within the still. Distillation is carried out with direct steam; depending upon the charge in the still and the steam pressure applied, distillation of one charge may require up to 20 hr. The distillation waters may require cohobation.

Peelings and shavings of the rhizomes constitute an excellent material for distillation, giving a good yield of oil, provided distillation is carried out immediately after peeling.

Physicochemical Properties of the Essential Oil.—The volatile oil derived from dried ginger is a mobile (viscous on aging!), greenish to yellowish liquid, possessing the characteristic aromatic odor, but not the pungent flavor ("bite"), of the spice. The odor of the oil is quite lasting.

Gildemeister and Hoffmann [14] reported these properties for oil of ginger:

Specific Gravity at 15°	0.877 to 0.886; oils of lower and higher specific gravity have been observed, however
Optical Rotation	−26° 0′ to −50° 0′ Lower rotations have been observed, however. For example, an oil distilled from old roots that had been stored for a long time, exhibited d_{15} 0.8924 and α_D −16° 58′
Refractive Index at 20°	1.489 to 1.494
Acid Number	Up to 2
Ester Number	Up to 15
Ester Number after Acetylation	24 to 50
Solubility	Only sparingly soluble in alcohol. Up to 7 vol. of 95% alcohol are required for solution, which is not always clear. In 90% alcohol the oils are generally, but not always, completely soluble

Genuine oils of ginger distilled by Fritzsche Brothers, Inc., New York, and under the author's supervision in Southern France (Seillans, Var) exhibited properties varying within the following limits:

Specific Gravity at 15°/15°	0.876 to 0.884, occasionally as high as 0.896

	Clevenger		*Kenworthy* *		*Lubell*	
	1	*2*	*1*	*2*	*1*	*2*
Yield of Oil (cc. per 100 g. of spice)..	3.25	1.39	2.46	1.22	3.30	1.37
Specific Gravity at 25°/25°.....	0.879	0.884	0.888	0.884	0.879	0.884
Optical Rotation at 25°.....	−42° 12′	−32° 12′	−21° 48′	−16° 36′	−41° 6′	−35° 30′
Refractive Index at 20°.....	1.491	1.493	1.494	1.495	1.492	1.494
Acid Number.....	2.93	4.29	2.6	4.8	3.5	3.46
Ester Number.....	11.02	18.7	35.3	25.3	16.03	17.7

* Kenworthy carried out his assays ten months after the ginger had been ground and stored in sealed glass jars. According to Clevenger, the results obtained by all three of the workers mentioned can be considered satisfactory. The variations in data reported are probably accounted for by the differences in time elapsed between grinding of the ginger and the assay of the material.

The Imperial Institute [16] in London steam-distilled dried ginger *peelings* from Sierra Leone and obtained 4.0 per cent of essential oil (I); Varier [17] submitted air-dried scrapings of northern Travancore ginger to water distillation and obtained 0.8 per cent of oil (II). The two oils had the following properties:

	I	*II*
Specific Gravity.....	d_{15}^{15} 0.881	d_{30} 0.8905
Optical Rotation.....	−43° 45′	−5° 12′
Refractive Index.....	n_D^{20} 1.492	n_D^{30} 1.4859
Acid Number.....	1.5	0.9
Ester Number.....	2.9	6.1
Ester Number after Acetylation.....	33.1	72.2
Solubility in 95% Alcohol at 15°.....	Soluble in 4 vol. and more	...

In various fractions of the oil which he investigated, Varier [18] noted the presence of *camphene*, *β-phellandrene*, and *zingiberene*.

Chemical Composition of Ginger Oil. The early investigations of ginger

Schimmel & Co.,[23] Dodge,[24] Brooks,[25] Ruzicka and van Veen,[26] Soffer and his collaborators,[27] and still more recently by Eschenmoser and Schinz.[28] The following compounds have been reported as constituents of the oil:

n-Decylaldehyde. In the forerun of the oil, Dodge noted the presence of an optically inactive aliphatic aldehyde d_{15} 0.828, which he believed to be *n*-decanal; it gave an oxime m. 63°, and a semicarbazone m. 98°. The odor of the aldehyde was reminiscent of orange peel oil. Since the melting points of the derivatives obtained by Dodge were not identical with those of pure *n*-decanal, it is possible that Dodge had isolated a mixture of *n*-decanal and *n*-nonanal.

n-Nonylaldehyde. That *n*-nonanal actually occurs in the oil was shortly afterward reported by Brooks.

d-Camphene. The terpene fraction b. 155°–165° of the oil exhibits dextrorotation (α_D +63° 13′), whereas the oil itself is laevorotatory (see above). In the terpene fraction Bertram and Walbaum identified *d*-camphene by hydration to isoborneol m. 212°, and by preparation of the bromal compound m. 71°.

d-β-Phellandrene. In the fraction b. 170° of the oil Bertram and Walbaum identified β-phellandrene by means of its nitrite m. 102°. More recently West [29] reported the presence of *d*-β-phellandrene in African ginger oil. West characterized this terpene by preparation of the nitrosochloride and the nitrosite; oxidation yielded 4-isopropyl-2-cyclohexen-1-one.

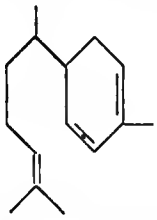
Methyl Heptenone. Reported as a constituent of the oil by Brooks.

Cineole. Identified by Schimmel & Co.; iodol compound m. 112°.

d-Borneol. Also identified by Schimmel & Co. (m. 204°, acid bornyl phthalate m. 164°), and later confirmed by Brooks.

Geraniol(?). Schimmel & Co. noted that the oil contains another alcohol, probably

Vol. II (and suggested by Soffer et al.[30]) has recently been declared erroneous by Eschenmoser and Schinz,[31] who have postulated the following configuration for zingiberene:



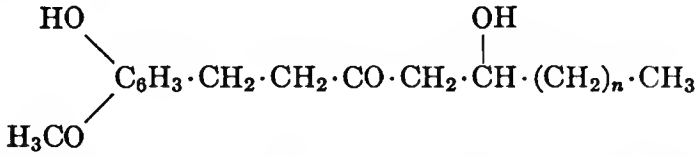
Zingiberol. According to Brooks, this sesquiterpene alcohol $C_{15}H_{26}O$ imparts to the oil its mild characteristic odor. From 150 g. of terpeneless and sesquiterpeneless ginger oil, Brooks isolated 24 g. of zingiberol $b_{14.5}$ 154°–157°. On heating, zingiberol lost water with simultaneous formation of a sesquiterpene $C_{15}H_{24}$, b. 255°–257°, which was either zingiberene or isozingiberene (cf. Vol. II of the present work, pp. 87, 91 and 261).

Use.—Oil of ginger is employed widely in the flavoring of all kinds of food products, particularly baked goods, confectionery, and spicy table sauces. It finds limited use also in perfumery, where it imparts an individual note to compositions of the oriental type.

Oleoresin Ginger

As with black pepper, the volatile (essential) oil derived by steam distillation of ginger represents only the aromatic, odorous constituents of the spice; it does not contain the nonvolatile, pungent principles for which ginger is so highly esteemed. To obtain all of these constituents in concentrated form, ground ginger is percolated with volatile solvents—acetone, alcohol, or ether. Concentration of the solution and careful removal of the solvent *in vacuo* yield the so-called oleoresin of ginger, in which the full pungency of the spice is preserved. The quantitative composition of the oleoresin depends upon the solvent used. Oleoresin of ginger (commercially known also as "Gingerin") generally contains these compounds:

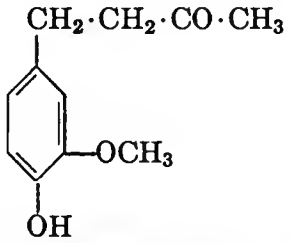
Nomura [33] extracted ginger with ether and, on subsequent treatment with alkali, obtained a substance with a very pungent flavor, which appeared to be a ketone and which he named *"Zingerone."* Almost simultaneously Lapworth, Pearson and Royle,[34] and Nelson [35] found that zingerone occurs in ginger not as free ketone, but in the form of compounds in which the ketone is a product of condensation (in molecular proportions) with saturated aliphatic aldehydes, principally enanthaldehyde (*n*-heptanal). Gingerol, a very pungent yellow oil, appears to be a mixture of homologues of this type:



In the chief homologue *n* seems to be 5, in other homologues *n* is 3 or 4.

On treatment of gingerol with alkali (as in the method of extraction employed by Nomura—see above) decomposition takes place, and free ketone (zingerone) is formed.

According to Nomura,[36] zingerone $C_{11}H_{14}O_3$, m. 40°–41°, possesses the following structural formula:

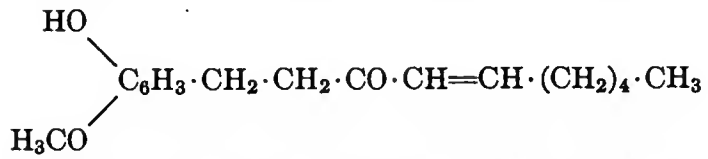


1-[4-Hydroxy-3-methoxyphenyl]-3-butanone

Zingerone has been synthesized by Mannich and Merz.[37]

2. *"Shogaol."* Nomura and his collaborators [38] isolated another pungent substance from ginger, which they named *"Shogaol"* (from the Japanese term "Shoga" for ginger). Shogaol $C_{17}H_{24}O_3$, a homologue of zingerone, has this structural formula:

[33] *J. Chem. Soc.* **111** (1917), 769.
[34] *Ibid.*, 777.
[35] *J. Am. Chem. Soc.* **39** (1917), 1466.
[36] *Science Repts. Tôhoku Imp. Univ.* [1], **6** (1917), 41.
[37] *Arch. Pharm.* **265** (1927). 15. Cf. Cotton. U. S. Patent 2.381.210. August 7. 1945.



[4-Hydroxy-3-methoxyphenyl]-ethyl-*n*-α,β-heptenyl Ketone

Shogaol can be synthesized from zingerone and hexaldehyde.

3. Aside from the pungent principles mentioned above, oleoresin of ginger also contains the volatile oil of ginger.

4. Unidentified resins are also contained in the oleoresin.

Suggested Additional Literature

R. Tzucker and C. B. Jordan, "A Study of the Assay of Ginger," *J. Am. Pharm. Assocn., Sci. Ed.* **29**, No. 6 (1940), 265.

Morris B. Jacobs, "Pungent Compounds Used in Flavoring," *Am. Perfumer* **48** (July 1946), 60.

THE CURCUMA OILS

Oil of *Curcuma Longa* L.

There are several species of the genus *Curcuma* (fam. *Zingiberaceae*), native to southeastern Asia, the tuberous roots of which contain a valuable yellow coloring principle (curcumine). One of the most important of these species is the common curcuma, *Curcuma longa* L., the dried tubers of which are used also for the flavoring of spicy native dishes. The plant is cultivated in India (Madras, Bombay, Bengal),[1] southern China, Formosa, Java, and the Philippines. On steam distillation the dried tubers yield from 1.3 to 5.5 per cent of an essential oil. (Rupe and collaborators[2] claimed that steam distillation of the dried tubers gives at the most 2 per cent of oil; Dieterle and Kaiser[3] reported a yield of 3.5 per cent from the rhizomes of *Curcuma domestica* Valeton.) The essential oil referred to in literature and in the trade as "Oil of Curcuma" is produced from *Curcuma longa* L.

[1] Re cultivation in India, see *Chemist Druggist* **88** (1916), 953.

Physicochemical Properties.—The volatile oil derived from the tubers of *Curcuma longa* L. is an orange-yellow, occasionally slightly fluorescent liquid, with an odor reminiscent of the tubers.

According to Gildemeister and Hoffmann,[4] the oil has these properties:

Specific Gravity at 15°	0.938 to 0.967
Optical Rotation	−13° 0′ to −25° 0′, or dextrorotatory up to +28°[5]
Refractive Index at 20°	1.512 to 1.517
Acid Number	0.6 to 3.1
Ester Number	6.5 to 16
Ester Number after Acetylation	28 to 53
Solubility	Soluble in 4 to 5 vol. of 80% alcohol; soluble in 0.5 to 1 vol. of 90% alcohol

Chemical Composition.—Oil of *Curcuma longa* has been the subject of numerous chemical investigations. The early works of Bolley, Suida and Dembe,[6] Kachler,[7] and Flückiger[8] require no discussion here because they gave no tangible results. Jackson and collaborators[9] isolated as chief constituent a substance of the empirical molecular formula $C_{13}H_{18}O$ or $C_{14}H_{20}O$, $b_{11\text{-}12}$ 158°–163°, $[\alpha]_D$ + 24° 35′, which they believed to be an alcohol and named turmerol. Later Rupe and collaborators[10] investigated turmerol more thoroughly but could not isolate it in pure form. Whenever they treated this compound with metallic sodium, hydrogen chloride or phosphorus trichloride, they obtained curcumone, a ketone $C_{12}H_{16}O$, which Rupe and Wiederkehr[11] succeeded in synthesizing.

(Curcumone is a slightly viscous liquid with a sharp odor reminiscent of ginger. It has these properties: $b_{8\text{-}11}$ 119°–122°, d_{20} 0.9566, $[\alpha]_D^{20}$ + 80° 33′; phenylhydrazone m. 92°, *m*-bromophenylhydrazone m. 71°, hen-

oil was made in 1934, when Rupe, Clar, Pfau and Plattner,[12] and Kelkar and Rao [13] found that more than 50 per cent of the oil consists of turmerone (see below). These two groups of researchers reported the presence of the following compounds in the oil derived from the tubers of *Curcuma longa* L.:

d-*α*-Phellandrene. In the lowest boiling fraction; first identified by Schimmel & Co.,[14] later confirmed by Luksch.[15] Nitrite m. 108°. Kelkar and Rao reported that the oil contains about 1 per cent of *d*-*α*-phellandrene.

d-Sabinene. About 0.6 per cent (Kelkar and Rao).

Cineole. About 1 per cent (Kelkar and Rao).

Borneol. About 0.5 per cent (Kelkar and Rao).

Zingiberene. About 25 per cent (Kelkar and Rao).

Sesquiterpene Alcohols(?). Rupe et al.[16] found that 5.9 per cent of the oil consists of sesquiterpene alcohols. Kelkar and Rao,[17] on their part, reported that the oil contains approximately 9 per cent of tertiary alcohols $C_{15}H_{24}O$ or $C_{15}H_{20}O$ which, on boiling with alkali, yield curcumone (see above).

Turmerone and *ar*-Turmerone. According to the two last-named authors, about 58 per cent of the oil is composed of a mixture of sesquiterpene ketones $C_{15}H_{22}O$ or $C_{15}H_{20}O$, the so-called turmerones.

Examining the turmerones more thoroughly, Rupe and collaborators found that the chief fraction (about 59 per cent) of the oil consists of 50 per cent of turmerone (an alicyclic sesquiterpene ketone $C_{15}H_{22}O$) and of 40 per cent of *ar*-turmerone (an aromatic ketone $C_{15}H_{20}O$). Cf. Vol. II of the present work, p. 450.

ar-Turmerone has been prepared synthetically by Colonge and Chambion,[18] and by Mukherjee.[19]

α- and *γ*-Atlantone. Rupe and collaborators reported the presence of small quantities

Physicochemical Properties.—Steam-distilling the triturated rhizomes, Rao, Shintre and Simonsen [20] obtained 6.1 per cent of a greenish-brown oil with a camphoraceous odor, exhibiting these properties:

Specific Gravity at 30°/30°	0.9139
Specific Optical Rotation at 30°	−12° 30′
Refractive Index at 30°	1.5001
Acid Number	0.9
Ester Number	2.03
Ester Number after Acetylation	58.66

Chemical Composition.—Rao, Shintre and Simonsen [21] identified the following compounds in the oil:

d-Camphene (0.8%). Characterized by means of its hydrochloride m. 149°–150°.

d-Camphor (2.5%). Identified by its melting point 175°, and by means of its oxime m. 118°.

Sesquiterpenes (65.5%, chiefly *l*-Curcumene). A few years after the first investigation, Rao and Simonsen [22] studied *l*-curcumene more thoroughly and found that it consists of two isomeric monocyclic sesquiterpenes $C_{15}H_{22}$, viz., *l*-α- and *l*-β-curcumene (cf. Vol. II of this work, p. 89).

Sesquiterpene Alcohols (22%). These alcohols b$_7$ 142°–144°, and b$_7$ 152°–154° are

Steam-distilling dried rhizomes of *Curcuma domestica* Valeton imported from Indonesia, Dieterle and Kaiser [24] obtained 3.5 per cent of a yellowish oil (d 0.941, α_D^{20} −19° 18′, n_D^{20} 1.5025) which had a peculiar odor and a burning taste.

Meijer and Koolhaas [25] found that the rhizomes of *Curcuma xanthorrhiza* Roxb. contained a maximum of volatile oil (and curcumine) at the beginning of their development. In the course of a year the oil content varied between 7.3 and 29.5 per cent, calculated upon the dried rhizomes. The highest yield of oil was obtained in October.

Physicochemical Properties.—Meijer and Koolhaas [26] reported these properties for the volatile oils of *Curcuma xanthorrhiza* Roxb., which they had obtained in the course of their investigation:

Specific Gravity at 27.5°/4°	0.9099 to 0.9250
Optical Rotation at 27°	−9° 0′ to −14° 40′
Refractive Index at 26°	1.5024 to 1.5079

Chemical Composition.—Dieterle and Kaiser [27] identified the following compounds in the volatile oil derived from the dried tubers of *Curcuma domestica* Valeton:

d-Camphor (1%). Characterized by means of its monobromide m. 76°.

Cyclo-isoprenemyrcene (85%). The chief constituent, identified by means of the hydrochloride m. 83°.

p-Tolylmethylcarbinol (5%). The medicinally active principle. Characterized by preparation of the phenylurethane m. 97.5°.

Meijer and Koolhaas [28] reported that the volatile oil from *Curcuma*

	Per Cent
d-α-Pinene	18
Ocimene	47.2
Linaloöl	11.2
Linalyl Acetate	9.1
Safrole	9.3
Unidentified Substances	3.5
Loss during Distillation	1.7

The oil is not produced on a commercial scale.

Oil of *Curcuma Caesia* Roxb.

Steam-distilling the air-dried and powdered rhizomes of *Curcuma caesia* Roxb. (fam. *Zingiberaceae*), Dutt [30] obtained about 1.5 per cent of a volatile oil (which in India is called "Kachri oil"). On standing, *d*-camphor crystallized from the oil. The rectified oil was dextrorotatory and had a pronounced camphoraceous odor. The following compounds were identified

Refractive Index at 20°	1.50233 to 1.50882
Acid Number	0.3 to 2.4
Ester Number	16 to 22.4
Ester Number after Acetylation	56 to 73.4
Solubility	Soluble in 1.5 to 2 vol. of 80% alcohol

Steam-distilling the dried and powdered rhizomes of *Curcuma zedoaria* Roscoe, Rao, Shintre and Simonsen [32] obtained 0.94 per cent of a viscous dark green oil with these properties:

Specific Gravity at 30°/30°	0.9724
Refractive Index at 30°	1.5002
Acid Number	1.3
Saponification Number	3.0

Acid Number	Up to 4
Ester Number	12 to 17
Ester Number after Acetylation	40 to 64
Eugenol Content	3 to 4%
Solubility	Miscible with 0.2 to 0.5 vol. and more of 90% alcohol; soluble in 10 to 25 vol. of 80% alcohol

Oils of galangal distilled by Fritzsche Brothers, Inc., New York, from imported root material had properties varying within these limits:

Specific Gravity at 15°/15°	0.913 to 0.923
Optical Rotation	−3° 5′ to −6° 50′
Refractive Index at 20°	1.4770 to 1.4810
Saponification Number	12.6 to 14.0
Solubility at 20°	Soluble in 0.5 vol. and more of 90% alcohol

Steam-distilling rhizomes of *Alpinia officinarum* Hance in East India, Rao and collaborators [2] obtained 0.3 per cent of an oil with the following properties:

Specific Gravity at 30°/30°	0.9061
Specific Optical Rotation at 30°	+3° 24′
Refractive Index at 30°	1.4801
Acid Number	2.6
Ester Number	19.1
Ester Number after Acetylation	78.0%

The odor of this oil was camphoraceous.

Chemical Composition.—The chemical composition of oil of galangal was investigated by Schimmel & Co.,[3] Schindelmeiser,[4] Fromm and Fluck,[5] and more recently by Ruzicka, Capato and Huyser.[6] The following compounds

A Compound $C_{10}H_{16}O$(?). Fromm and Fluck isolated 1 to 2 per cent of a substance $C_{10}H_{16}O$, b. 208°–210° which, however, was not identified.

A Sesquiterpene(?). From the fraction b. 230°–240°, Schindelmeiser obtained a viscous dihydrochloride $C_{15}H_{24}\cdot 2HCl$, m. 51°, b_{10} 145°–150°.

A Sesquiterpene(?). Fromm and Fluck isolated a sesquiterpene b_{12-15} 138°–140°, which contained two double bonds, and added four atoms of bromine. Since this sesquiterpene does not react with gaseous hydrogen chloride, it was not identical with that described by Schindelmeiser (see above).

A Sesquiterpene(?). Fromm and Fluck isolated another sesquiterpene which yielded a

Acid Number	1.8
Ester Number	145.6
Solubility	Soluble in 1 vol. of 80% alcohol; opalescent on addition of 3 vol. of 80% alcohol

Chemical Composition.—Another oil from Salatiga was investigated by Ultée,[10] who reported the presence of the following compounds:

d-Pinene. Presence probable.

Cineole (20–30%). Characterized by means of its iodol compound m. 112°.

Camphor. M. 170°–175°.

Methyl Cinnamate (48%). M. 34°.

Use.—Oil of *Alpinia galanga* is not produced on a commercial scale.

OIL OF *KAEMPFERIA GALANGA* L.

Kaempferia galanga L. (fam. *Zingiberaceae*) is cultivated in Malaya and India. The dried rhizomes, known in Java as "Kentjoer" or "Tjekoer," are used in Malaya for medicinal purposes and for the flavoring of curries; in

Chemical Composition.—The chemical composition of oil of *Kaempferia galanga* L. was investigated by van Romburgh[3] and by Panicker, Rao and

OIL OF PEPPER

Essence de Poivre Aceite Esencial Pimienta Negra Pfefferöl

ous short roots; by means of these latter the vine clings to its support, which may be either a pole of hard, rot-resistant wood with a rough surface, or a

Ester Number	11.0 to 16.6
Solubility	Soluble in 0.5 vol. of 95% alcohol, opalescent to cloudy with more

Chemical Composition.—The chemical composition of oil of mastic was investigated by Flückiger,[2] and by Schimmel & Co.,[3] who found that oil of mastic contains *d-α-pinene,* and a small percentage of optically inactive *α-pinene.* Aside from pinene, another terpene appears to be present in the oil, but it has not yet been characterized.

Production and Use.—Only very small quantities of oil of mastic are produced commercially. The oil finds limited use in flavoring compounds, particularly in certain liqueurs.

Suggested Additional Literature

G. Reinboth, "Producing Oils and Resins in Italy," *Farbe u. Lack* (1938), 364. *Chem. Abstracts* **32** (1938), 9532.

[2] *Arch. Pharm.* **219** (1881), 170.
[3] Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 203.

Digitized by Google
Original from CORNELL UNIVERSITY

OIL OF SANDALWOOD EAST INDIAN

Essence de Santal des Indes *Ostindisches Sandelholzöl*
Aceite Esencial Sandalo Indias Orientales *Oleum Ligni Santali*

Botany and Occurrence.—The common term "Sandalwood" refers to trees belonging to several plant families and genera. There was much controversy among taxonomists over the classification of the various types of sandalwood trees before their identity was clearly established. (Cf. the monograph on "Oil of Sandalwood, West Indian," Vol. III of this work, p. 385, and the following monograph on "Oil of Sandalwood, Australian" in the present volume, p. 187.)

By far the most important sandalwood oil is that distilled from the roots and heartwood of *Santalum album* Linn. (fam. *Santalaceae*) an evergreen tree almost entirely confined to the forests of Mysore (southern India) and closely adjacent districts. This—the East Indian sandalwood oil—differs in chemical composition and odor from other, so-called sandalwood oils, which are derived from entirely different trees.

According to Sastry,[1] sandalwood as such is used for religious purposes in India by the Hindus and Parsis; as perfume materials, the wood as well as the oil have been favorites from time immemorial. History tells us of caravans passing over the deserts of Persia, Arabia, and Asia Minor carrying Indian sandalwood to Egypt, Greece, and Rome. It has been perhaps one of the most precious perfumery materials from antiquity down to modern times, and its popularity has shown no signs of waning.

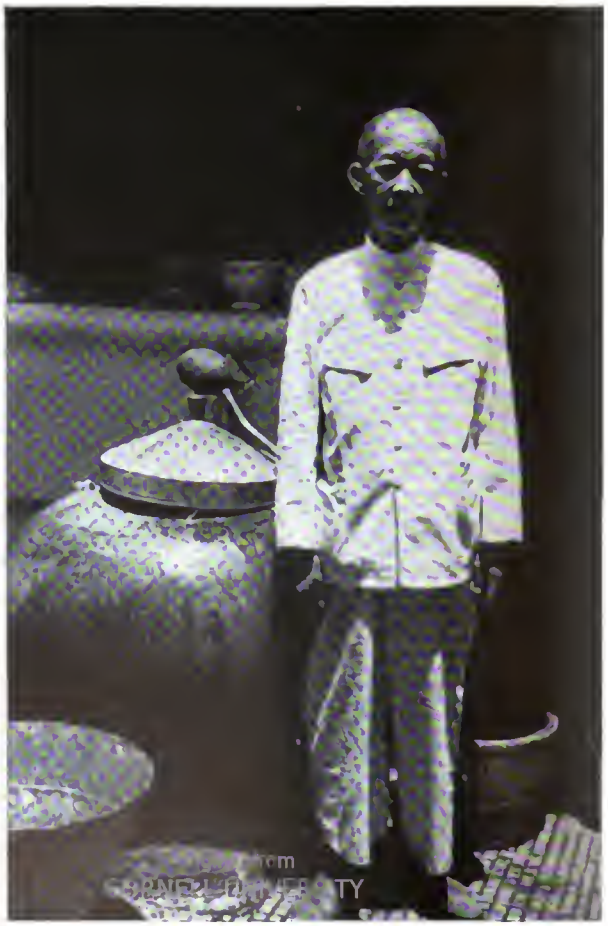
Santalum album L. is a native of the highlands of southern India and the Malayan Archipelago. It occurs ferally in open dry places, preferably at altitudes ranging from 2,000 to 3,000 ft. It is also planted (by seed), particularly in the State of Mysore, the principal producing region of the wood and essential oil. The tree, which may attain a height of 60 to 65 ft., is actually an obligate hemiparasite plant. Soon after germination of the seed, the roots attach themselves to those of nearby grasses, herbs, bushes, and undergrowth in general, obtaining food by means of the haustorium, and finally causing the host plants to perish. As the sandalwood tree grows, essential oil develops in the root and heartwood. (In this connection it should be mentioned that occasionally a tree may reach physiological ma-

[1] *J. Sci. Ind. Research* **3**, No. 2 (1944), 1.

Digitized by Google Original from CORNELL UNIVERSITY

(*Top*) Production of balsam copaiba in the lower Amazon Basin, State of Pará, Brazil. A hole is drilled into the lower part of the trunk, from which the balsam will flow. (*Right*) Production of balsam Peru in El Salvador, C. A. "Cascara Process": Incisions are made in the trunk of a tree, after it has been scorched with a torch flame. (*Bottom Left*) Balsam Peru, El Salvador, C. A. "Trapo Process": Burlap is hammered into the incisions to absorb the flowing balsam. (*Bottom Right*) Balsam Peru, El Salvador, C. A. "Trapo Process": A bundle of burlap soaked with balsam and removed from the incisions. *Photos Fritzsche Brothers, Inc., New York.*

(*Top Left*) Production of cananga oil in the Bantam region of Java (Indonesia). Collection of the flowers with long hooked bamboo poles. (*Top Right*) Cananga oil, Bantam region. A small boy climbing into the tree with a long bamboo pole to reach the flowers. (*Bottom Left*) Cananga oil, Cheribon region of Java (Indonesia). The harvesters climb up the tall trees on a sort of bamboo ladder. (*Bottom Right*) Cananga oil, Cheribon region. A wealthy Chinese broker who purchases the bulk of the oil from the native distillers. *Photos Fritzsche Brothers, Inc., New York.*



Digitized by Google

According to Sastry,[2] the total amount of sandalwood distilled varies from 2,500 to 3,000 tons a year, depending on the demands for sandalwood oil and other economic factors. Accurate statistics are not easily available.

A published account[3] indicates the following quantities of distillation material processed in 1927–28 in India (Mysore and Bangalore factories), and in New York:

Class of Wood	*India (in tons)*	*New York (in tons)*	*Total (in tons)*
Roots.....	306	...	306
Billets.....	240	299	539
Jajpokal.....	408	75	483
Sandal chips.....	78	...	78
Milwa chilta.....	612	...	612
	1,644	375	2,021

(Figures approximate)

From this wood the two government factories in Mysore distilled 167,720 lb. of sandalwood oil; 45,840 lb. were distilled in New York. The average yield of oil varied from 105 to 110 lb. per ton of wood.

Habitat.—According to information gathered by the author[4] while surveying production of sandalwood oil in the south of India, *Santalum album* L. thrives on well-drained, loamy soil. It grows also on laterite, but not waterlogged ground, and preferably on slopes of hills exposed to the sun. It requires a minimum of 20 to 25 in. of rainfall per year; more than 80 in. is harmful. The finest wood, as regards odor, grows in the driest regions, particularly on red or stony ground. On rocky ground the tree often remains small, but gives the highest yield of oil. It grows most abundantly in the dry-deciduous belt along the banks of the Cauvery River, among the mountains which run through the State of Mysore from north to south. Trees more than thirty years old may have a circumference of from 18 to 38 in. The bark and the sapwood are odorless; the roots and heartwood contain the essential oil.

As has been pointed out, *Santalum album* is a parasite which attaches its roots to those of neighboring plants. In this respect the tree has certain preferences, its most suitable hosts being *Cassia siamea, Pongamia glabra* and *Lantana acuminata.* Less suited are *Bassia latifolia, Dalbergia, Sissoo* and *Fiecus* species. Experiments regarding the most suitable host

[2] *Ibid.*

[3] E. J. Parry, "Sandalwood Oil," a monograph published by the government of Mysore.

[4] The author is greatly indebted to Mr. S. G. Sastry, former Director of Industries and Commerce in Mysore, now retired in Bangalore, and to Dr. M. N. Ramaswami, Mysore Government Sandalwood Oil Factory, Mysore, for their kindness in correcting the present monograph, and bringing all information up-to-date.

Digitized by Google Original from CORNELL UNIVERSITY

plants are still being carried out by the forest service of Mysore State. If all neighboring hosts were removed, the roots of *Santalum album* would stretch out farther and farther in search of sustenance, until, finding none, the tree would perish.

Propagation.—In years past the sandal tree occurred mainly in the wild state, but reckless exploitation and the danger of losing the great revenue from forests induced the Mysore Government to restrict the cutting, and to propagate large numbers of trees every year (by sowing). At one time propagation of the sandal tree was considered a difficult matter, but the problem has been much simplified, thanks to the experimental work of the forestry department of Mysore.

A certain amount of propagation takes place by means of birds. The blue-colored fruit of the tree is juicy and sweet and much liked by birds, which eat the outer fleshy part and drop the hard seed. Falling on suitable soil, this seed germinates, taking root and, unless destroyed by its natural enemies, grows into a tree. In past years this was the only way the sandal tree was propagated.

Today most sandal trees, at least in the State of Mysore, are propagated by sowing. The seed is placed directly into the ground, because the delicate nature of the root, which must prey on a host root, does not permit transplanting of the young trees from a nursery. The sowing is done about two weeks before the arrival of the monsoon rains, usually at the end of April. Since not all seeds germinate, five seeds are planted in a semicircle and surrounded by a number of host plants. A great enemy of the sandal tree is the common rat, which burrows into the ground for food and eats the seed. Therefore, the seed is given a protective coating of red lead paste prior to planting. The young plants grow very slowly. Foraging goats frequently attempt to feed on it and may destroy it, but the dense, thorny foliage of the surrounding host plants protects the young and tender sandal tree.

The gravest peril to the sandal tree is the so-called spike disease. This is extremely dangerous because of its contagious nature, and also because no remedy has as yet been found. It represents a kind of "plant consumption," the nature of which is not fully understood. It is possible to infect a healthy sandalwood tree by grafting a piece of wood from a diseased tree upon it; soon after, characteristic symptoms of the spike disease can be noticed—a sickly appearance, a grayish color, and under-development of the leaves, which remain small and curl up. Perhaps the spike disease is carried from one tree to another by insects. Whenever the forest service notices any sandal tree attacked by the disease, they immediately order it quarantined and destroyed. This is done by cutting a ring around the tree

Digitized by Google
Original from CORNELL UNIVERSITY

and painting the uncovered wood with a solution of arsenic trichloride in hydrochloric acid, or with a solution of sodium arsenate. The tree then dies in three to four weeks and the germs of the disease are destroyed. Experiments have proved that oil distilled from such treated trees contained no traces of arsenic.

Under normal conditions young sandal trees grow slowly, gradually developing a core of heartwood which, together with the root, contains the much valued essential oil. It is estimated that this core should be at least 3 in. thick before exploitation of the tree becomes worth while. To attain a thickness of 3 in. requires more than thirty years. The soft, white outer layer, the so-called sapwood, contains no essential oil and is therefore removed and discarded. The older the tree, the thicker its core of heartwood and the more value it has as fragrant sandalwood. Since the roots consist chiefly of heartwood, they are richest in essential oil. According to the classification established in 1898 there exist 18 grades of sandalwood, ranging from the heartwood down to the chips and sawdust. The grading refers to the physical condition of the wood, not its quality. An exact classification is given by Gildemeister and Hoffmann.[5] Today this grading has lost much of its former significance, probably because the bulk of sandalwood is now used in the government distillery of Mysore State for distillation of the oil. There is quite a sharp line of demarcation between the soft, white wood and the darker heartwood. The thickness and appearance of the heartwood, which are functions of age, are also considered. The darker the wood the higher is the oil content. Trees from mountainous, rocky, and dry soil develop the hardest wood and the greatest amount of oil. The thickest blocks of sandalwood are too valuable for distillation because they can be used more advantageously for wood carvings, or for cabinet making, but all the lower grades may serve for distillation, the only difference then being in regard to yield of oil. The roots yield up to 10 per cent of oil, while the intermediary layers between soft and hard wood give only about 2½ per cent. The yield may be as low as 1 per cent and even less, in chips which contain much sapwood. Chips and sawdust are frequently employed in incense.

Sandalwood Production in Mysore State.—Years ago, the government of Mysore enacted laws to stop the reckless exploitation of the sandalwood forests which threatened this source of revenue to the country. The entire sandalwood industry of the State of Mysore is now organized on the basis of a strict government monopoly. Laws and regulations governing the production and handling of sandalwood are equaled in strictness only by those which govern the mining of gold in other countries. Sandalwood and

[5] "Die Ätherischen Öle," 3d Ed., Vol. II, 504.

Digitized by Google Original from CORNELL UNIVERSITY

its oil represent gold to Mysore, favored as the state is with such an abundance of this tree.

In Mysore every single sandal tree belongs to the government, whether it be grown on public, private, or temple grounds. The law obliges every proprietor of land on which a sandal tree grows to give this tree the utmost care. No individual is permitted to cut a tree, possess, transport, or export sandalwood, or distill the wood without permission. Every single piece of wood which may serve for carving, for example, must carry the government stamp, certifying that it has been purchased from the government and that it is not stolen, or "bootleg" wood. Only dead or fully grown trees which show signs of death from old age may be felled, after permission has been granted by a government forest official. He, too, is subject to fines should he allow the felling of a healthy tree, unless it is done for experimental or scientific purposes. Similar regulations apply to the transport of sandalwood, with the result that today the Mysore Government has at its disposal an abundance of old sandal trees for the distillation of oil or for the export of wood. In addition, the Mysore forestry service has embarked on a long-range program of replanting a certain acreage with sandal trees each year, so that the future supply of this valuable wood may be assured; in fact, it should be almost inexhaustible. Only 15 miles outside of the State of Mysore one sees large tracts of land covered with young sandalwood trees. The reforestation program of the government is carried out thoroughly and efficiently, and taking into consideration all kinds of possible adversities—weather, for instance, which might in some years prevent the development of newly planted trees. By strict laws regulating cutting and transporting, the sandalwood remains government property throughout the various phases from sowing of the seed to export of the wood, or marketing of the oil distilled in the government-owned factory.

The actual felling of the tree is not done by the government; the forest officials merely mark the trees which may be cut. The work is then assigned to the lowest bidding party who enters contracts to cut and transport the wood to the government stations. Contractors comprise organized groups of woodsmen whose expenses consist chiefly of labor charges and maintenance costs for bullocks and carts. Since the government pays the contractors only by weight of material received, woodcutters would prefer to fell only the trunks, the pulling of the root being a much more difficult job. However, the forestry service requires that for each trunk the corresponding root, too, must be delivered and that the wood must be shipped in long pieces. Too much sawdust would be lost if the wood were cut into small segments in the forests. It is also unlawful to remove the soft, white sapwood on the spot, and to haul only the heartwood to the government stations, because the stacking up in the forests of the valuable and less

Digitized by Google
Original from CORNELL UNIVERSITY

bulky heartwood is risky. Hence the transported sandalwood must have a layer of at least ½ in. of sapwood around the heartwood. This measure has been enacted chiefly to provide a certain protection against theft at night or en route; moreover, it protects the valuable core of sandalwood from mechanical injury during the transport.

The felled sandalwood trees and the pulled roots are transported first by bullock carts through the more inaccessible sections of the forests, subsequently by motor trucks over the highways, and finally by railroad to the warehouses of the forest service. These latter are distributed throughout the producing regions. Because of possible theft, guards patrol the forests, and every forest official has the right to stop and search any suspicious vehicle. Sandalwood readily betrays itself by its pronounced odor, for which reason some thieves try to hide the stolen wood in sacks of coriander seed or onions. Such tricks, however, are well known to the forestry inspectors. Guards patrol also the state line of Mysore to prevent the smuggling out of stolen wood.

The first step in the operations performed in government warehouses is the removal of the outer layer of sapwood by crews of men and women. All work is carried out under strict supervision, and only a minimum of waste is permitted in the sawing and chipping of the wood. Chips and sawdust are carefully collected and used for distillation, or sold for use in incense. Finally, the forestry department sells the wood to the Mysore Government Sandalwood Oil Factory, a mere book transaction because all the wood belongs to the government. Wood which is not used for distillation is sold or auctioned off, and transported by rail to Bombay or other ports, from where it is shipped to all parts of the world.

The State of Mysore annually produces about 2,000 tons of sandalwood, the bulk of which serves for distillation of oil in the Mysore Government factory; 10 or 12 per cent of the tonnage is sold and exported chiefly for wood carving and use in incense. Throughout India, sandalwood powder is burned in religious rites. The Hindus cremate their dead and use sandalwood in the burial pyres, while the fire-worshiping Parsis also employ much sandalwood powder in incense. The above-mentioned figure of 2,000 tons is only an average, because the government restricts cutting according to actual requirements for wood and oil, which can be anticipated quite closely by years of experience in marketing the oil throughout the world.

Wood and Oil Production in Coorg and Madras.—Next to the State of Mysore the most important producers of sandalwood in India are the neighboring Province of Coorg and the Presidency of Madras. In Coorg and Madras the cutting of sandalwood is also regulated, but much less strictly than in Mysore. Any trees growing on private land are the property of the owner and may be cut and sold freely. Auctions of sandalwood

Digitized by Google Original from CORNELL UNIVERSITY

are held regularly in Fraserpett, Tirupatur, and Satayamangalam. However, these auctions have lost much of their former importance, because very little oil is produced today outside of India. (The one exception is the oil distilled in New York by the sole agents of the Mysore Government Sandalwood Oil Factory, from wood shipped from Mysore. This is done merely because of United States tariff considerations. Sandalwood enters the United States free of duty, whereas the oil is subject to an import tax.) Essential oil houses in Europe and in the United States determined to distill their own oil would have to import the wood either from Coorg or Madras, or from the island of Timor in the Malayan Archipelago (see above).

There are two small sandalwood distilleries in Kuppam (Madras Presidency) which have been operating for more than twenty years, one factory at Bombay, one at Kanauj, one at Mettur, and one at Karaikal. The average output of oil in the Mysore factory is about 120,000 lb. per year, the maximum capacity being 50 per cent more. The output of all the other factories in India is about 40,000 to 50,000 lb. a year.

Distillation.—Sastry [6] has given a detailed account of the distillation of sandalwood, as carried out today in India. The following description is based chiefly upon his experience as Director of Industries and Commerce, Mysore, and as Director of the Mysore Government Sandalwood Oil Factory.

The distillation of sandalwood oil in India has been carried on from very ancient times by the so-called water distillation method (cf. Vol. I of the present work, pp. 112, 120, 142). It consists in soaking the raw material in water in a copper vessel and heating it on an open fire. The vapors from the body of the still are conducted through a bamboo or copper pipe to receivers which are kept in cold water, the latter being renewed frequently. Even today such methods of distillation are practiced on the Malabar Coast and also in some places in northern India, notably in Kanauj. If the method is conducted with care and vigilance, it is still possible to obtain a high quality sandalwood oil, even though the yield may be somewhat low. Many old-fashioned *attar* distillers in Kanauj still prefer sandalwood oil prepared by the old-fashioned water distillation method. This oil is claimed to possess a finer odor than the oil produced in modern steam stills.

In modern operation the raw material consists of billets and roots of sandalwood and also a quantity of chips, the latter being a mixture of both the heartwood and the sapwood. The yield of oil varies, the roots giving the highest percentage and the chips the least. The average yield from good billets and roots ranges between 4.5 to 6.25 per cent.

[6] *J. Sci. Ind. Research* **3**, No. 2 (1944), 1.

Digitized by Google Original from CORNELL UNIVERSITY

The wood is first of all fed to a chipping machine consisting of a rapidly rotating disc on which are mounted 6 knives radially; the wood pressed against these knives gets reduced into a coarse powder. The latter is next fed to disintegrators which will reduce the wood into a finer state of division. In some of the factories, the chipper is avoided and manual labor employed to chop the wood by means of hatchets and adzes into small-sized sticks or chips. These are then fed into disintegrators. The powder that comes from the disintegrator is carefully sieved and remixed with the object of obtaining a powder that will not "pack in" too tightly in the stills but will form a uniform porous body of material which admits of the passage of steam easily over the entire mass of powder to be distilled.

The stills, usually made of copper, rarely of iron, are provided with goosenecks to conduct the vapor of the oil and steam to tin-lined tubular condensers. The receivers, also tin-lined, are constructed on the principle of the old Florentine flasks. The size and shape of the stills vary, but the standard equipment is a still holding a charge of ¾ to 1 ton of powdered wood, the latter being generally placed on a perforated false bottom. There is usually a little space on the top of the "burden" in the still. The height of the still is about 25 per cent more than the diameter. Stills with a height very much greater than the diameter are also in use but require a careful distribution of the powder inside, as otherwise the steam will have a tendency to force an easy passage without spreading itself uniformly over the entire mass of the powder.

Distillation generally requires 48 to 72 hr. Each factory, according to its economic conditions, has its own end point of distillation. The latter is stopped when the yield of oil ceases to be economical. The distillate collects in the receivers, the crude sandalwood oil floating on the surface. This is generally skimmed off with the help of shallow ladles and then put into a separating funnel where oil and water layers are further separated. The crude oil is stored in a separate vessel and allowed to stay in this condition for some time when a little scum with suspended woody matter comes to the top. The oil is then carefully filtered.

Distillation is usually conducted with low pressure steam, anywhere between 20 to 40 lb. High-pressure steam has been recommended for sandalwood oil distillation on the score of a slightly higher yield of the oil and a slight saving in time. Obviously, high-pressure steam means higher temperature and the delicacy of the odor of some of the constituents will suffer at higher temperatures. Orthodox opinion favors low-pressure distillation, some factories in England and America using steam only at 10-lb. pressure, even today.

In many factories in India adopting the method of steam distillation

Digitized by Google Original from CORNELL UNIVERSITY

mentioned above, the oil does not receive any further treatment. At best, it is warmed once again in order to drive out most of the moisture contained in the oil and filtered once again. Such oil is marketed straight away as "Perfumery grade of oil." It has been stated that many of the *attar* manufacturers in India have no objection to the use of this oil in their preparations. Some of this oil is also exported to western countries where it is further rectified. There have been instances where by careful distillation of selected wood the oil obtained in the above manner comes within the range of pharmacopoeial standards, but there is no certainty about this.

If the oil is to conform to the pharmacopoeial standards of the different countries of the world, it should be carefully analyzed in the laboratory and further rectified. Very often this necessitates a distillation with superheated steam and final heating in a steam-jacketed vacuum still to remove the last traces of water, and also vacuum filtration. The oil finally obtained has a pale yellow color, is optically clear, and possesses the characteristic odor of sandalwood. By adopting the above methods it will be easy to produce a standard product day after day, with a certainty and a guarantee that the product will strictly conform to the rigid pharmacopoeial standards.

The first modern sandalwood oil factory to be established in India was at Bangalore during the middle of World War I, and this was followed by another distillery at Mysore. The Bangalore factory was closed down after some time and all the operations are now concentrated in the city of Mysore. This plant is complete in every branch of mechanical and chemical engineering equipment. It has an up-to-date control laboratory. The factory makes its own condensers in the copper smithy section of the workshop. All the repairs and replacements are looked after by this workshop which has also a small foundry and a modern tin-can-making plant attached to it. The Mysore plant is the biggest and the most completely equipped sandalwood oil distillery in the world. During days of heavy production about 1,500,000 gal. of water circulate in the factory; the warm water flowing from the condensers is used again after it has been cooled in a sprinkling system and stored in large tanks. The exhausted wood is dried and used as fuel.

Packing.—The Mysore factory has set up a standard of packing sandalwood oil, and today more than 90 per cent of the oil on the world market is packed according to these specifications. This consists of a tin containing 25 lb. net of oil, after due allowances for ullage, each lot having a reference number. On the Indian market, the following other packings are also recognized: tins containing 10 and 5 lb.; aluminum bottles containing 1 lb., 8 oz., 4 oz., and 1 oz. For retail trade in India, 1-oz. aluminum con-

Digitized by Google Original from CORNELL UNIVERSITY

tainers are very popular and nearly 3 to 4 lakhs of these containers are being used in the trade every year.

Physicochemical Properties.—The volatile oil derived from the roots and heartwood of *Santalum album* L. is a somewhat viscous, yellowish liquid of peculiar, "heavy," sweet, and very lasting odor, characteristic of East Indian sandalwood.

Gildemeister and Hoffmann [7] reported these properties for East Indian sandalwood oil:

Specific Gravity at 15°	0.973 to 0.985
Optical Rotation	−16° 0′ to −21° 0′; in exceptional cases lower rotations have been observed
Refractive Index at 20°	1.504 to 1.509
Acid Number	0.5 to 8.0 (see below)
Ester Number	3.0 to 17.0
Ester Number after Acetylation	Not less than 196
Total Alcohol Content, Calculated as Santalol	Not less than 90% (see below)
Solubility at 20°	Soluble in 3 to 5 vol. and more of 70% alcohol; in 5 to 6 vol. and more of 69% alcohol; in 6 to 7 vol. and more of 68% alcohol (see below)

On these properties Gildemeister and Hoffmann [8] elaborate as follows:

Oils produced by the old-fashioned method of water distillation may exhibit a higher acid number than indicated above. The acid number can be reduced by fractionation of the oil, and by removal of the foreruns which contain teresantalic acid.

The higher its santalol content, the greater is the value of an oil. Oils of best quality exhibit a santalol content of 94 per cent and even more.

In the solubility test the solution must remain clear on further addition of solvent. Turbidity, however, is not necessarily proof of adulteration; it may be caused by the presence of decomposition or resinification products. These may be the result of improper distillation, or of age, the oil losing its originally normal solubility under the influence of air and light.

Oils produced by the old method of water distillation in primitive native stills often exhibit a dark color, an abnormally high specific gravity, and occasionally an empyreumatic odor. East Indian sandalwood oils with a high specific gravity have been known for a long time.[9] Warming sandalwood oil with water of 50° for ten days, Conroy [10] reported that the specific gravity increased from 0.975 to 0.989.

Genuine East Indian sandalwood oils examined by Fritzsche Brothers, Inc., New York, in the course of years had properties varying within the following limits:

[7] "Die Ätherischen Öle," 3d Ed., Vol. II, 508.
[8] *Ibid.*
[9] *Chemist Druggist*, May 26, 1894.
[10] *Ibid.*, August 19, 1893.

Digitized by Google
Original from CORNELL UNIVERSITY

Specific Gravity at 25°/25°	0.969 to 0.975, sometimes as high as 0.979
Optical Rotation	−15° 0′ to −19° 20′
Refractive Index at 20°	1.5052 to 1.5077
Ester Content, Calculated as Santalyl Acetate	1.6 to 5.4%
Total Alcohol Content, Calculated as Santalol	90.3 to 97.4%
Solubility	Soluble in 3.5 to 5 vol. and more of 70% alcohol

A type sample of an oil produced and examined in the Mysore Government Sandalwood Oil Factory (April 1944) exhibited these values: [11]

Specific Gravity at 15.5°	0.9782
Optical Rotation at 20°	−17° 6′
Refractive Index at 20°	1.5068
Ester Content, Calculated as Santalyl Acetate	2.5%
Free Alcohol Content, Calculated as Santalol	91.2%
Solubility	Soluble in 5 vol. of 70% alcohol

Adulteration.—Present specifications of the various pharmacopoeias make it quite difficult to adulterate East Indian sandalwood oil to any considerable extent, without seriously affecting its properties. Formerly, oils of cedarwood, guaiac wood, West Indian, West Australian and South African sandalwood, and oils of copaiba balsam and gurjun balsam were used for this purpose. Addition of cedarwood oil or gurjun balsam oil increases the optical rotation, and decreases the specific gravity and solubility of the sandalwood oil. Copaiba balsam oil acts similarly, except that it usually decreases the rotation slightly. West Indian sandalwood oil is dextrorotatory and quite insoluble in dilute alcohol. West Australian sandalwood oil has a lower specific gravity, a lower laevorotation, and if not rectified, a lower ester number after acetylation, and poorer solubility than the East Indian oil. Its odor differs from that of the East Indian oil. Addition of most of the above-named oils to an East Indian oil will lower the santalol content of the latter, which should be 90 per cent or more in high-grade oils. To simulate a high alcohol content, synthetics and aromatic isolates such as terpineol, benzyl alcohol, or geraniol are occasionally used. They can be detected by acetylation of the oil; benzyl acetate and geranyl acetate will betray themselves by a fruity note in the odor of the acetylized oil. The presence of terpinyl acetate can be proved by fractional saponification of the acetylized oil for 1 hr. and 2 hr. (cf. Vol. I of this work, p. 336). A suspected oil should be submitted to fractional distillation *in vacuo;* any adulterants boiling lower than santalol can easily be separated.

[11] Sastry, *J. Sci. Ind. Research* **3**, No. 2 (1944), 1.

Digitized by Google Original from CORNELL UNIVERSITY

According to Sastry,[12] white paraffin oil has lately been observed as an adulterant of East Indian sandalwood oil. It can be detected by the so-called "Oleum Test" described in Vol. I of this work, p. 332.

A careful odor test is indispensable in the analysis of East Indian sandalwood oil.

Chemical Composition.—The chemical composition of the volatile oil derived from the root and heartwood of *Santalum album* L. has been the subject of numerous investigations. Details regarding the various constituents identified in the oil will be found in the respective monographs contained in Vol. II of the present work. The chief constituent, amounting to 90 or more per cent of the oil, is *santalol*, a mixture of two primary sesquiterpene alcohols $C_{15}H_{24}O$, viz., α- and β-santalol, in which the α- form predominates.

The presence of the following compounds has been reported in East Indian sandalwood oil:

Isovaleraldehyde. In the foreruns of the oil. Identified by means of the thiosemicarbazone m. 49°–53°. Aside from isovaleraldehyde, the oil contains other aldehydes b. 50°–130° (Schimmel & Co.[13]).

Santene. Observed by Müller [14] in the low boiling fractions of the oil (cf. Vol. II of this work, p. 79).

Nortricycloekasantalane(?). In the foreruns of the oil Schimmel & Co.[15] noted the presence of a completely saturated hydrocarbon $C_{11}H_{18}$, b. 183°, d_{15} 0.9133, d_{20} 0.9092, α_D −23° 55′, n_D^{20} 1.47860, which is probably identical with Semmler's nortricycloekasantalane. At room temperature the hydrocarbon was not affected by potassium permanganate solution.

l-Santenone. Müller [16] first reported that the foreruns b. 180°–200° of East Indian sandalwood oil contain a ketone, the semicarbazone of which melted at 224°. Later, Schimmel & Co.[17] proved that this ketone is identical with the π-norcamphor of Semmler and Bartelt,[18] and with the santenone of Aschan [19] (cf. Vol. II of this work, p. 438).

Santenone Alcohol (Santenol). In the fraction b. 196°–198°. (For details see Vol. II of this work, p. 229.)

Teresantalol. In the fraction b. 210°–220°. (For details see Vol. II, p. 257.)

Nortricycloekasantalal. In the fraction b. 222°–224°. First isolated by Schimmel & Co.[20] (Cf. Vol. II, p. 350.)

[12] *Ibid.*
[13] *Ber. Schimmel & Co.*, October (1910), 98.
[14] *Arch. Pharm.* **238** (1900), 366.
[15] *Ber. Schimmel & Co.*, October (1910), 102.
[16] *Arch. Pharm.* **238** (1900), 372.
[17] *Ber. Schimmel & Co.*, October (1910), 98.
[18] *Ber.* **40** (1907), 4465; **41** (1908), 125.
[19] *Ber.* **40** (1907), 4918.
[20] *Ber. Schimmel & Co.*, October (1910), 103.

Digitized by Google Original from CORNELL UNIVERSITY

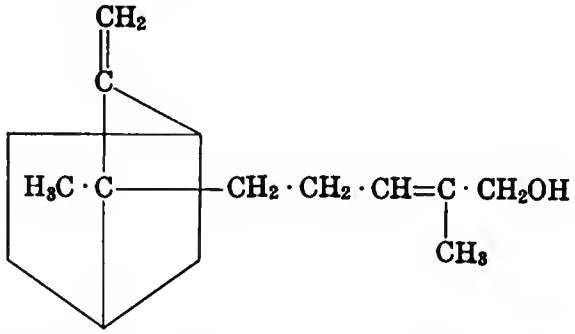
Santalone. In the fraction b. 213°–216°. (For details see Vol. II, p. 494.)

A Ketone(?). The same fraction contains another ketone $C_{11}H_{16}O$, which is probably isomeric with santalone. Semicarbazone m. 208°–209°, oxime m. 97°–99°.

α- and β-Santalene. The occurrence of sesquiterpenes in East Indian sandalwood oil was first reported by von Soden and Müller.[21] Shortly afterward Guerbet [22] showed that these hydrocarbons are two isomers, which he named α- and β-santalene (cf. Vol. II, pp. 112 ff.).

α- and β-Santalol. The chief constituent of the oil, amounting to 90 or more per cent. In the mixture of α- and β-santalol present in the oil, the α-isomer predominates. The characteristic odor, as well as the medicinal value of East Indian sandalwood oil, is a result of the presence of the santalols (for details see Vol. II, pp. 265 ff.).

In 1947, Bhattacharyya [23] suggested the following structural formula for β-santalol:



Santalal(?). According to Chapoteaut,[24] and Guerbet,[25] the aldehyde $C_{15}H_{22}O$, obtained by oxidation of santalol, occurs in East Indian sandalwood oil as a natural constituent. However, this has not been proved conclusively.[26]

Semmler and Bode [27] oxidized santalol with chromic acid in glacial acetic acid and obtained an aldehyde $C_{15}H_{22}O$, the properties of which are described in Vol. II of the present work, p. 267.

Teresantalic Acid. First reported by Müller.[28] It occurs in the oil partly free, partly in esterified form (cf. Vol. II, p. 113).

Santalic Acid. First reported by Guerbet [29] (for details see Vol. II, p. 611).

According to Müller,[30] the oil contains still other acids which, however, have not yet been identified.

[21] *Pharm. Ztg.* **44** (1899), 258. *Arch. Pharm.* **238** (1900), 363.
[22] *Compt. rend.* **130** (1900), 417.
[23] *Science Culture* **13** (1947), 158. *Chem. Abstracts* **43** (1949), 5382.
[24] *Bull. soc. chim.* [2], **37** (1882), 303.
[25] *Ibid.* [3], **23** (1900), 540, 542. *Compt. rend.* **130** (1900), 417, 1324.
[26] Cf. Chapman and Burgess, *Proc. Chem. Soc.* (1896), 140. Chapman, *J. Chem. Soc.* **79** (1901), 134.
[27] *Ber.* **40** (1907), 1124; **43** (1910), 1722.
[28] *Arch. Pharm.* **238** (1900), 374.
[29] *Compt. rend.* **130** (1900), 417, 1324. *Bull. soc. chim.* [3], **23** (1900), 540, 542.
[30] *Arch. Pharm.* **238** (1900), 374.

Digitized by Google
Original from CORNELL UNIVERSITY

Phenols(?), Lactones(?) and Borneol(?). Von Soden and Müller[31] noted in the oil phenols of strong and disagreeable odor and lactones of fruity odor. None of these has been identified. According to the same authors, the oil probably also contains borneol in free and in esterified form. In the opinion of Gildemeister and Hoffmann,[32] it is quite possible that the borneol-like odor noted by von Soden and Müller may have been caused by santenone alcohol, which was later detected in the oil (see above).

Use.—During the early part of the twentieth century a large portion of the sandalwood oil produced in the world was used for medicinal purposes, particularly for the treatment of certain diseases, gonorrhea among them. Today the situation is entirely changed, only about 10 per cent serving for medicinal purposes. Natives in Asia still use the oil for self-treatment. In modern medical practice sandalwood oil has been replaced by the sulfa drugs, and by certain antibiotics.

As regards the perfume, cosmetic and soap industries, East Indian sandalwood oil is one of the most important ingredients. No composition of the heavy or oriental type is complete without an ample dose of this oil. Its sweet, powerful and lasting odor makes it an excellent fixative in the scenting of soaps. About 90 per cent of the East Indian sandalwood oil produced today is used in perfumes, cosmetics and soaps.

SANDALWOOD OILS AUSTRALIAN[1]

A. Oil of *Eucarya Spicata* Sprag. et Summ.
(West Australian Sandalwood Oil)

History.—The story of Australian sandalwood oil is one of vicissitudes. The oil was first distilled experimentally in 1875 by Schimmel & Co. in Leipzig, Germany.[2] It is difficult to determine exactly when Australian sandalwood oil was placed on the market; however, fifty years ago there was sporadic production of the oil by a number of small distillers in Western Australia. At that time the oil was marketed in a crude state (prac-

[31] *Pharm. Ztg.* **44** (1899), 259.
[32] "Die Ätherischen Öle," 3d Ed., Vol. II, 517.
[1] This monograph by A. R. Penfold and F. R. Morrison, Museum of Applied Arts and Sciences, Sydney, Australia.
[2] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 521.

Digitized by Google Original from CORNELL UNIVERSITY

tically the same condition as that in which it was obtained by distillation of the wood), with the result that the santalol content was very low.

It is of interest to record that two well-known pharmacists played a prominent part in establishing the industry in Western Australia. According to Marr,[3] a Mr. Mayhew, when President of the Pharmaceutical Society of Western Australia, spent a considerable sum of money in distilling and marketing the oil in 1894–95; the late E. J. Parry, of essential oil fame, started operations in the Mount Barker district many years ago. C. L. Braddock produced the oil from time to time between 1916 and 1923.

It was not until 1921 that systematic production and scientific control of the oil were instituted by Plaimar Ltd.,[4] Perth, Western Australia. Since then the quality of the Western Australian sandalwood oil has been greatly improved; in fact, to such a degree that the oil is now recognized as being the equivalent of the well established and better known East Indian sandalwood oil. It was the great increase in its actual santalol content, and the fact that the Western Australian oil was at least equal therapeutically to the East Indian oil that resulted in its inclusion in the British Pharmacopoeia of 1932.

The improved status of the oil has been reflected in a larger demand; production increased from 3,720 lb. in 1920 to over 120,000 lb. in 1932. The volume has since dropped, however, to about 30,000 lb. per year, largely because distillers have been unable to obtain sufficient supplies of wood.

It is difficult to discuss sandalwood oil without reference to the wood itself, for the earliest record of shipment shows that 4 tons of wood, valued at £50, were exported to the Far East in 1846. The logs (stick wood) are shipped to Eastern Asia for use in incense; for the production of sandalwood oil in Western Australia chiefly roots and butts are used.

Until the adoption of the licensing system by the Western Australian Government, large tracts of forests were denuded of sandalwood, the logs being shipped to eastern markets. At the present time sandalwood can only be collected under license. Prior to World War II, the export value of Australian sandalwood logs was about £30 per ton. The continuous demand for the wood over the years has greatly reduced the existing areas of growth, and sandalwood cutters must now travel long distances for supplies. This fact, together with an increased demand from the Far East after World War II, caused the price of the wood to rise to a figure far in excess of its value for distillation purposes. The production of the oil in Australia, therefore, declined substantially. Since the Australian oil must compete on the world market with the East Indian sandalwood oil,

[3] Private communication from Mr. H. V. Marr, Perth, Western Australia.
[4] Penfold, *Australasian J. Pharm.* **18** (1937), 154.

Digitized by Google
Original from CORNELL UNIVERSITY

the price of the wood in Australia must be sufficiently low to permit economical operation.

Botany.—Australian sandalwood oil is obtained from the heartwood of a diminutive tree or large bush, of straggly habit, about 12 to 20 ft. in height, with a trunk 6 to 10 in. in diameter. It occurs in the arid regions of Western and South Australia. The tree is now classified as *Eucarya spicata* (R. Br.) Sprag. et Summ.[5] (syn. *Santalum spicatum* [R. Br.] A. DC.), fam. *Santalaceae.*

The Western Australian sandalwood tree has had very rough handling by scientific botanists. It was first known as *Santalum spicatum* or *S. zygnorum.*. This was later changed to *Fusanus spicatus*, and finally to *Eucarya spicata.*[6] This last classification was accepted by the British Pharmacopoeia in 1932, but synonymized as *Santalum spicatum.* The effects of a change in botanical nomenclature upon a commercial product are far-reaching, and the treatment accorded Australian sandalwood oil offers a typical example. For some years Australian sandalwood oil suffered severely in competition with the East Indian oil, because merchants used differences in nomenclature and chemical composition for trade purposes. The complete change of name from the genus *Santalum* to the genus *Eucarya* created the erroneous impression that the Australian oil was entirely different in chemical composition and in therapeutical properties from the East Indian sandalwood oil.

Method of Production.—The commercial process has been stated to be one of solvent extraction and steam distillation of the concentrated extract. Depending upon geographical origin of the tree and method of extraction the yield of oil varies between 1.4 and 2.6 per cent. According to the British Pharmaceutical Codex of 1949, Australian sandalwood oil is obtained by distillation *and rectification* (italics by the authors) from the wood of *Eucarya spicata* Sprag. et Summ.

Physicochemical Properties.—Australian sandalwood oil is a colorless or light yellow, somewhat viscous, liquid with a strong and lasting odor characteristic of the wood.

The oil exhibits these properties:

Specific Gravity at 15.5°/15.5°	0.970 to 0.976
Optical Rotation	−3° 0′ to −10° 0′
Refractive Index at 20°	1.498 to 1.508
Free Alcohol Content, Calculated as Santalol	Not less than 90% (in commercial, i.e., rectified oils)
Solubility at 20°	Soluble in 3 to 6 vol. of 70% alcohol

[5] Sprague and Summerhayes, *Kew Bull. Misc. Information* **5** (1927), 195.
[6] Penfold, *J. Proc. Roy. Soc. N. S. Wales* **70** (1936), 23.

Digitized by Google Original from CORNELL UNIVERSITY

According to certificates of analyses of recent shipments from Perth to Europe,[7] the physicochemical properties of commercial (rectified) Australian sandalwood oil vary within the following limits:

Specific Gravity at 15.5°/15.5°...	0.969 to 0.9725
Optical Rotation.....	−3° 0′ to −5° 0′
Refractive Index at 20°.....	1.505 to 1.506
Total Alcohol Content, Calculated as Santalol.....	94.3% to 95.4%
Solubility at 20°.....	Soluble in 3 to 3.5 vol. of 70% alcohol

Chemical Composition.—Commercial sandalwood oil from Western Australia contains more than 90 per cent of sesquiterpene alcohols, calculated as $C_{15}H_{24}O$. These alcohols have been the subject of much controversy (see "The Fusanols," Vol. II of the present work, p. 269). Their nature was not established until 1925, when Penfold [8] identified *α-santalol* as chief constituent, by preparation of its allophanate m. 162°–163°, by oxidation with chromic acid to santalal (semicarbazone m. 230°), and by oxidation with potassium permanganate solution to tricycloekasantalic acid m. 76.5°. The actual santalol content of the crude (unrectified) oil does not fall below 60 per cent.

The constitution of the other alcohols present in the oil has not yet been elucidated (cf. Vol. II of the present work, p. 270), but present investigations by Penfold are proceeding slowly. A *primary sesquiterpene alcohol* (b_{2-3} 137°–138°, d_{15}^{15} 0.9353, α_D −0° 30′, n_D^{20} 1.5034) [9] has been isolated. So far, no crystalline derivatives of this alcohol have been prepared. The same is true of a *secondary sesquiterpene alcohol* (b_1 145°–150°, d_{15}^{15} 0.994 to 0.995, α_D +18° 24′ to +26° 12′, n_D^{20} 1.5100 to 1.5106), which is also under investigation.

The oil furthermore contains a small percentage of *bisabolene*, which Schimmel & Co.[10] identified in the lowest boiling fraction by means of the trihydrochloride m. 79.7° to 80.5°.

In this connection it should be noted that recently Treibs [11] reported that the last runs of the Australian, but not of the Indian, sandalwood oils contain glycols and hydroxy-oxido derivatives of the sesquiterpene group. The well-known crystalline "santal camphor" (see Volume II of the present work, p. 768) of the *South* Australian sandalwood oil (*Santalum preissianum* Miq.) is a bicyclic oxido-sesquiterpene alcohol with a long side chain, hence of a structure similar to that of *β*-santalol.

Use.—The earliest use of Australian sandalwood oil was for therapeutical purposes. It is still being employed medicinally, contrary to general belief.

[7] Private communication from Plaimar Ltd., Perth, Western Australia.
[8] *J. Proc. Roy. Soc. N. S. Wales* **62** (1928), 60.
[9] Unpublished data.
[10] *Ber. Schimmel & Co.* (1921), 43.
[11] *Chem. Ber.* **84** (1951), 47.

Digitized by Google
Original from CORNELL UNIVERSITY

According to Marr,[12] supplies of Australian sandalwood in capsules and in 1-lb. bottles are still shipped to China, the Malayan Archipelago, and South America where it is largely used for self-medication.

The oil is employed also in perfumes, cosmetics, and for the scenting of soaps. It possesses a heavy, powerful, and very lasting odor which blends particularly well with perfume compositions of the oriental type.

B. Oil of *Santalum Lanceolatum* R. Br.

Introduction and Botany.—The botany of this tree has been fully discussed by Bentham.[13] The tree occurs in New South Wales, Queensland, and in the northwestern part of Western Australia. The essential oil derived from the wood of this tree was used at one time to bring the optical rotation of commercial Australian sandalwood up to the requirements demanded by various pharmacopoeias. However, the entire amount of oil produced from *Santalum lanceolatum* has never exceeded 5 per cent of the total output of Australian sandalwood oil.

On steam distillation the comminuted wood yields from 2 to 2.5 per cent of oil.

Physicochemical Properties.—Oil of *Santalum lanceolatum* is of unusual chemical interest, as it differs entirely from the oil of *Eucarya spicata*. The properties of the oil vary within these limits:

Specific Gravity at 15°/15°	0.9474 to 0.9628
Optical Rotation	−45° 42′ to −61° 0′
Refractive Index at 20°	1.5068 to 1.5085
Ester Number	8.4 to 23.5
Ester Number after Acetylation	200 to 205
Solubility	Soluble in 1.3 to 1.7 vol. of 70% alcohol

Chemical Composition.—Oil of *Santalum lanceolatum* contains no santalol. The chief constituent is a primary, highly laevorotatory sesquiterpene alcohol $C_{15}H_{24}O$ (b_5 163°–165°, d_{15}^{15} 0.9474, α_D −66° 42′, n_D^{20} 1.5074; allophanate m. 114°–115°, strychnate m. 103°–105°) which was isolated in 1928 by Penfold,[14] and later named *lanceol* by Bradfield, Francis, Penfold and Simonsen.[15] (Cf. Vol. II of the present work, p. 270.) Lanceol does not appear to be structurally related to α- or β-santalol. For details of its chemical reactions and a discussion of its probable constitution the reader

[12] Private communication from Mr. H. V. Marr, Perth, Western Australia.
[13] "Flora Australiensis," Vol. VI, London (1873), p. 214.
[14] *J. Proc. Roy. Soc. N. S. Wales* **62** (1928), 70.
[15] *J. Chem. Soc.* (1936), 1619.

Digitized by Google Original from CORNELL UNIVERSITY

may consult the original literature. Recently, Eschenmoser, Schreiber and Keller [16] advanced a probable structural formula for lanceol, which is a primary, monocyclic sesquiterpene alcohol containing three double bonds.

Use.—Oil of *Santalum lanceolatum* is not produced commercially at present.

C. Oil of *Eremophila Mitchelli* Benth.[17]

Introduction and Botany.—No account of Australian sandalwood oil would be complete without some reference to the so-called "Bastard Sandalwood" or "Buddah," *Eremophila mitchelli* Benth., a tall shrub, or small tree, belonging to the fam. *Myoporaceae.* The tree attains a height of 20 to 30 ft., with a maximum diameter of 12 in. at the butt, and bears a wealth of white, scented flowers in the spring. It is one of the strongest scented woods of Australia.

Eremophila mitchelli occurs in the arid regions of New South Wales, Queensland, and South Australia. The tree, very common in Western Queensland, is often confused with *Santalum lanceolatum,* both trees being known as sandalwood.

The stick wood (logs), after reduction to shavings, yield from 2 to 3 per cent of a dark colored viscous oil with a pleasant and characteristic odor.

Physicochemical Properties.—The properties of oil of *Eremophila mitchelli* vary within these limits:

Specific Gravity at 15°/15°	1.03 to 1.04
Optical Rotation	+6° 0′ to −6° 0′
Refractive Index at 20°	1.5260 to 1.5384
Solubility	Soluble in 2 to 4 vol. of 70% alcohol

Chemical Composition.—Oil of *Eremophila mitchelli* contains three closely related sesquiterpene ketones, which were isolated by Bradfield, Penfold and Simonsen.[18] The discovery of these three ketones in oil of *Eremophila mitchelli* is probably the first record of their occurrence in nature. The ketones are:

Eremophilone	$C_{15}H_{22}O$, m. 42°–43°, $[\alpha]_{5461}$ −207°
2-Hydroxyeremophilone	$C_{15}H_{22}O_2$, m. 66°–67°, $[\alpha]_{5461}$ +153°
2-Hydroxy-2-dihydroeremophilone	$C_{15}H_{24}O_2$, m. 102°–103°, $[\alpha]_{5461}$ +94°

[16] *Helv. Chim. Acta* **34** (1951), 1667.
[17] "Flora Australiensis," Vol. V, London (1870), p. 21.
[18] *J. Chem. Soc.* (1932), 2744. *J. Proc. Roy. Soc. N. S. Wales* **66** (1932), 420.

Digitized by Google
Original from CORNELL UNIVERSITY

Regarding the structural formulas and details pertaining to these sesquiterpene ketones, see Vol. II of the present work, p. 451.

Use.—Oil of *Eremophila mitchelli*, although dark in color, possesses marked blending and fixative properties valuable in the scenting of soap and technical preparations. While the oil is not so useful as genuine sandalwood oil, it nevertheless has remarkable qualities, which place its value in line with those of the fixative balsams.

OIL OF SANDALWOOD AFRICAN
(*Osyris* Oil)

Little is known about the so-called "African Sandalwood Oil" and its botanical origin. About sixty years ago, Schimmel & Co.[1] distilled wood imported from Tamatave (Madagascar) and obtained 3 per cent of a ruby-red oil (d_{15} 0.969), the odor of which resembled that of the so-called West Indian sandalwood oil. The wood was perhaps identical with that of *Osyris tenuifolia* Engl. (see below), or with the so-called "Hasoranto Wood"[2] from northern Madagascar.

Distilling "East African Sandalwood Oil," probably derived from *Osyris tenuifolia* Engl. (fam. *Santalaceae*),[3] Schimmel & Co.[4] obtained 4.86 per cent of a light-brown oil with an odor similar to that of vetiver and gurjun balsam oils, but very different from that of East Indian sandalwood oil. The oil had these properties:

Specific Gravity at 15°	0.9477
Optical Rotation	−42° 50′
Refractive Index at 20°	1.52191
Ester Number	11.1
Ester Number after Acetylation	72.8
Total Alcohol Content, Calculated as $C_{15}H_{26}O$	30.5%
Solubility	Not readily soluble; soluble in 7 to 8 vol. of 90% alcohol

[1] *Ber. Schimmel & Co.*, April (1891), 49.
[2] Sawer, "Odorographia," London (1892), Vol. I, 325.
[3] Cf. A. Engler and G. Volkens, "Über das wohlriechende ostafrikanische Sandelholz (*Osyris tenuifolia* Engl.)," *Notizblatt des Königl. botan. Gartens und Museums*, Berlin, No. 9, Aug. 7, 1897.
[4] *Ber. Schimmel & Co.*, October (1908), 111.

Digitized by Google Original from CORNELL UNIVERSITY

Haensel [5] described two so-called East African sandalwood oils of unknown botanical origin. They were probably distilled from the same plant material as the *Osyris* oils. The two oils exhibited the following properties:

	I	*II*
Specific Gravity at 20°	0.9589	0.9630
Optical Rotation	−40° 36′	−60° 58′
Acid Number	1.7	...
Saponification Number	17.9	8.1
Ester Number after Acetylation	88.3	68.6

These oils contained a sesquiterpene b_{747} 263.5°–265°, d_{20} 0.9243, α_D −32° 55′, and a sesquiterpene alcohol b_{25} 186°–188°.

More recently, Schimmel & Co.[6] examined an African sandalwood oil of unknown botanical origin and found these properties:

Specific Gravity at 15°	0.9637
Optical Rotation	−45° 56′
Refractive Index at 20°	1.50762
Acid Number	0.7
Ester Number	7.5
Ester Number after Acetylation	203.5
Total Alcohol Content, Calculated as $C_{15}H_{26}O$	95.2%
Solubility	Soluble in 4 vol. and more of 70% alcohol; slightly opalescent on addition of more alcohol

The oil resembled the above-mentioned *Osyris* oils.

Nothing is known about the actual production of this type of oil. According to Muller [7] no sandalwood oil is produced in Madagascar.

[5] *Chem. Zentr.* (1906), II, 1496; (1909), I, 1477.
[6] *Ber. Schimmel & Co.* (1938), 97.
[7] Private communication from Mr. Charles Muller, Ambanja, Madagascar.

Digitized by Google
Original from CORNELL UNIVERSITY

CHAPTER VII

ESSENTIAL OILS OF THE PLANT FAMILY *ZYGOPHYLLACEAE*

Digitized by Google

Original from
CORNELL UNIVERSITY

Digitized by Google

Original from
CORNELL UNIVERSITY

OIL OF GUAIAC WOOD

Botany, Origin and Production.—Strictly speaking, guaiac wood is the wood of *Guaiacum officinale* L. (*lignum vitae*) and of *G. sanctum* L. However, the wood of these species contains only small quantities of volatile oil. The commercial, so-called oil of guaiac wood is obtained today by steam distillation of the heartwood of *Bulnesia sarmienti* Lor. (fam. *Zygophyllaceae*), a tree 10 to 12 ft. high with a trunk diameter of about 10 in., and often gnarled and crooked in appearance. It grows wild and very abundantly throughout the Gran Chaco, the famed "Green Hell." This is a vast region consisting mostly of waterless scrub jungle, covering parts of Paraguay and Argentina and inhabited in part by wild Indian tribes. The wood of *Bulnesia sarmienti* Lor. resembles that of *Guaiacum officinale* L. and *G. sanctum* L. in being very hard; it is used for the making of fence posts, ornamental objects, and for the extraction of its volatile oil by steam distillation. The oil was first introduced on the market in 1891. Prior to World War II limited quantities of "Palo Santo" logs (as the tree is called locally) were shipped from the Gran Chaco, chiefly to Europe, for extraction of the essential oil. In 1935, for example, exports of logs from Paraguay and Argentina amounted to 257 metric tons, cost of transport being offset, at least partially, by the high yield of oil (5 to 6 per cent) obtained in the modern distilleries of Europe and North America. In 1938 a firm in Asunción, capital of Paraguay, started production of the oil, thus effecting a considerable saving in shipping costs. In this distillery the logs of "Palo Santo" trees are sawed mechanically into blocks, and then reduced to coarse sawdust by means of hogging machines, hammers and grinders, such as are employed in paper mills. The sawdust falls into a concrete basin sunk into the ground and filled with water. Two hundred and fifty pounds of coarse sawdust absorb approximately 750 lb. of water. The wetted distilla-

The yield of oil ranges from 2.7 to 3.0 per cent. In 1950 this plant produced about 6,000 kg. of oil.

Two other distilleries of guaiac wood, producing together about 11,000 kg. of oil per year, are located in the heart of the Gran Chaco, where the Mennonites in 1928 established a colony, which now numbers more than 8,000 people. The older of these two distilleries is situated in Filadelfia, the center of the colony, the other about 40 miles to the east of Filadelfia, right in the forests where the "Palo Santo" tree grows wild and abundantly. Because of the great number of trees still available, production of oil could be increased substantially if demand and price of the oil should warrant it. The trees are felled, and the logs pulled out of the forests by teams of oxen. Then the thick layer of bark and sapwood is removed, and the wood of the trunks and heavy branches is mechanically reduced to shavings. These are steam-distilled in quite primitive stills. Distillation of one charge lasts 12 hr.; work goes on day and night, and the yield of oil averages 3 per cent. Filter paper not being available, the warm liquid oil separated from the condensate is filtered through cotton. Obviously these two distilleries, in the heart of the Gran Chaco, can produce oil at a much lower cost than a distillery to which the logs must be hauled over long distances, out of the almost inaccessible forest region, partly by land over very poor roads, partly by river on lighters.

In this connection it should be noted that the condition of the wood appears to exert some influence upon the odor of the oil. The oil produced by the Mennonites in the growing region from freshly cut wood has an odor somewhat different from that of the oils distilled from old logs dried and aged during the long transport abroad.

Physicochemical Properties.—Oil of guaiac wood is a viscous liquid which, at room temperature, slowly congeals to a yellowish-white crystalline mass. Once solidified, it can be reliquefied at temperatures ranging from 40°–50° C. The oil has a pleasant, soft and mellow rose-like odor, resembling that of tea roses, and to a slight degree that of violets.

Gildemeister and Hoffmann [1] reported the following properties for oil of guaiac wood:

Specific Gravity at 30°	0.967 to 0.974

Guaiol Content	42 to 72%
Solubility	Soluble in 3 to 5 vol. of 70% alcohol

Genuine oils of guaiac wood imported by Fritzsche Brothers, Inc., New York, from Paraguay and Brazil had properties varying within these limits:

Specific Gravity Calculated at 15°/15°	0.974 to 0.983
Optical Rotation	−7° 9′ to −12° 16′
Refractive Index at 20°	1.5040 to 1.5080
Alcohol Content, Calculated as Guaiol	62.9 to 82.5%
Solubility at 20°	Soluble in 2 to 6.5 vol. and more of 70% alcohol

Distilling imported guaiac wood in Southern France, the author and his associates extended the time of distillation to 24 hr. and obtained yields of oil ranging from 4.8 to 5.37 per cent. It was found that yields up to 7.5 per cent, and a good quality of oil, could be obtained by thoroughly mixing the powdered wood with water, adding traces of sulfuric acid, and distilling the mass after it had been allowed to macerate overnight. Since the acid has a deteriorating effect upon the metal of the stills, the process is impractical unless glass-lined or wooden stills are employed.

Oils distilled in Seillans (Var), France, under the author's supervision had these properties:

Specific Gravity Calculated at 15°	0.973 to 0.978
Optical Rotation	−3° 30′ to −8° 48′
Refractive Index at 20°	1.5050 to 1.5059
Saponification Number	0 to 4.2
Ester Number after Acetylation	135.4 to 166.1
Total Alcohol Content, Calculated as Guaiol	59.8 to 75.2%
Solubility at 20°	Soluble in 3.5 to 4 vol. and more of 70% alcohol

Chemical Composition.—Relatively little is known about the chemical composition of the volatile oil derived from the wood of *Bulnesia sarmienti*, particularly in regard to its odoriferous principles. The presence of the following compounds has been reported:

Guaiol. A bicyclic, tertiary sesquiterpene alcohol $C_{15}H_{26}O$, containing one double bond. On dehydration it yields guaiene $C_{15}H_{24}$. When dehydrogenated with sulfur, guaiene gives deep blue guaiazulene $C_{15}H_{18}$ (for details re Guaiol, see Vol. II of this work, 278).

Bulnesol. Also a bicyclic, tertiary sesquiterpene alcohol $C_{15}H_{26}O$, containing one double bond (see Vol. II of this work, p. 756).

Digitized by Google Original from CORNELL UNIVERSITY

Use.—Oil of guaiac wood is an interesting perfumer's material, quite widely employed in rose compositions. Its principle merit lies in its lasting qualities, whence the use of the oil as a natural fixative of odors. Being moderately priced, oil of guaiac wood serves to good advantage in the scenting of soaps. It helps to conceal harsh notes of synthetic aromatics.

In years past, the oil was occasionally employed as an adulterant of Bulgarian and Turkish rose oils.

Digitized by Google
Original from CORNELL UNIVERSITY

CHAPTER VIII

ESSENTIAL OILS OF THE PLANT FAMILY *LEGUMINOSAE*

Digitized by Google

Original from
CORNELL UNIVERSITY

Digitized by Google

Original from
CORNELL UNIVERSITY

OIL OF BALSAM COPAIBA

Essence de Baume de Copahu *Copaivabalsamöl*
Aceite Esencial Balsamo Copaiba *Oleum Balsami Copaivae*

Balsam Copaiba

Botany and Origin.—Balsam [1] copaiba is the oleoresin obtained from the trunk of various species of the genus *Copaifera* L. (fam. *Leguminosae*), tall, multi-branched trees, with a large trunk and a smooth bark. The tree, a native of the northern part of South America, grows wild in the vast forests and jungles of Brazil (Amazon Basin), and to a lesser extent in Venezuela, Guiana, and Colombia.

The oleoresin originates probably by decomposition of the cell walls of the wood parenchyma. The schizogenous cavities within the wood and pith of the tree trunk, in which the copaiba accumulates, enlarge and join, forming reservoirs of surprisingly large capacity, which hold gallons of oleoresin. On tapping of the tree, the oleoresin flows from the wound as a clear, colorless, thin liquid which, however, soon acquires a thicker consistency and a yellowish tinge.

Literature cites a number of *Copaifera* species which produce copaiba balsam, but the taxonomy of the trees that are actually exploited is still somewhat confused. According to Freise,[2] who undertook a study of the subject, the genus *Copaifera* is represented in Brazil by fifteen species occurring in all states from the extreme north to São Paulo; but only the following species are of commercial interest:

(1) *Copaifera reticulata* Ducke.
70% of all Brazilian copaiba balsam originates from this species.
(2) *C. guianensis* (Desf.) Benth.
About 10% of the exported balsam comes from this species. It grows also in Guiana.
(3) *C. multijuga* Hayne.
About 5 per cent are collected from this species.

[1] The term "balsam" for copaiba is a misnomer since copaiba is actually an oleoresin. However, the term balsam will be retained in this monograph because the trade has become used to it in the course of many years.
[2] *Perfumery Essential Oil Record* **25** (1934), 218.

Digitized by Google
Original from CORNELL UNIVERSITY

(4) *C. officinalis* L.

Not more than 3 to 5 per cent of the exported copaiba is now derived from this species. It grows also in Venezuela, where it supplies the so-called Maracaibo balsam.

(5) *C. martii* var. *rigida* (Benth.) Ducke.

(6) *C. coriacea* (Mart.) Ktze.

The balsam from this species is exported mostly to Belem-Pará for admixture with better grades.

Of the different types of copaiba reaching the world market, the product from the middle and lower Amazon Basin is by far the most important. Commercially known as "Pará balsam," it includes also balsam from Manáos, a city located on the junction of the Amazon and the Rio Negro. Both products are shipped abroad from Belem-Pará, located in the Amazon Delta. Markets in North America, Europe and the Far East are supplied mainly with copaiba from the Brazilian states of Pará and Amazonas, and only seldom with that from Bahia.

Chief producing regions of balsam copaiba in Brazil are:

(a) State of Pará. These stretch over the lower Amazon Basin, mostly south of Belem-Pará. The trees grow in vast areas, along the larger tributaries of the Amazon, the smaller ones not yet being exploited. The southern tributaries are the Tocantins, Anapú, Pacajá, Xingú and Tapajoz. Production along some of the northern tributaries—e.g., the Parú, Jary, and Yamunda—is insignificant.

(b) State of Amazonas. As will be explained later, only the so-called insoluble balsam comes from this part of Brazil. Its insolubility probably results from soil conditions and from the very humid climate of this region. Here the balsam is collected chiefly along the banks of the Amazon and adjacent tributaries—e.g., the Madeira, Purus, Jurua, Rio Negro, and Rio Branco.

In all these areas there are no plantations, the copaiba trees growing wild in the somewhat drier sections of the jungles. Native woodsmen, financed by traders and exporters, exploit the trees. They refuse to be employed on a fixed wage basis and consider the job of day laborer beneath their dignity. Therefore, they prefer to work on their own.

balsam. The trees, which usually grow on dry land, may almost be compared with containers, being filled in the hollow center with oleoresin, which can easily be drawn from them. This is done simply by drilling two holes into the trunk, one 2 to 3 ft. above the ground, and the other 10 to 20 ft. higher. A bamboo tube, provided with a simple stopcock, is driven into the lower hole. Under normal conditions, the copaiba flows easily and as a clear liquid, particularly if the tree has not been tapped for several years. The product is then collected in cans. If the copaiba does not flow readily, a fire is made at the base of the trunk and at the elevated temperature the oleoresin will flow more easily. After completion of the tapping operation, both holes are closed with a simple plug.

The quality of copaiba drawn from each tree depends upon the botanical species of the tree, its age, the lapse of time since the previous tapping, and upon the season. On the average, a tree yields from about 17 to 18 kg. of copaiba balsam per year. In general, the trees are exploited all year around, provided production is stimulated by demand and sufficiently attractive prices. It must be borne in mind that it takes many days, and often weeks, of difficult traveling to reach the remote regions of production, and that so far away from civilization the cost of food, which must be carried along, increases enormously. The same holds true of the transport of the collected copaiba back to the trading centers.

The season of production depends, to a certain extent, upon the region and the prevailing weather. In most sections the best period for collecting the copaiba is in the dry months from July to November, because the trees then give the largest yield. During the rainy season, they contain very little oleoresin.

In the trading centers, the product is either sold to intermediaries for cash or bartered against food, clothing, and other necessities. Frequently, advances in the form of cash or food are made to the workers by traders or exporters in Belem-Pará or Manáos. Accounts are then settled by delivery of copaiba balsam and other products of the jungles to the trading posts. The crude product is subsequently shipped by boat down the rivers to

The State of Pará produces both soluble and insoluble copaiba; the State of Amazonas supplies only insoluble copaiba. Sixty per cent of the exports from Pará are of the soluble, and about 40 per cent of the insoluble, type. Thus Brazil supplies much larger quantities of insoluble copaiba than of soluble copaiba. The difference in price usually varies from 10 to 50 per cent.

Solubility of the copaiba has no relation to its color and specific gravity; nor is solubility a criterion for purity and odor of the product. The solubility simply offers a means of distinguishing between the two commercial types of copaiba. Exporters in Brazil apply no other tests. No attention is paid to specific gravity or other properties, which appear to vary with the trees exploited, their age, the region of production, the time of collection, and other factors. The odor of the different lots is quite similar, at least in regard to the pure, unadulterated product. Some attention is paid to the color, because certain countries specify a light color, while others are less particular in this respect. To summarize, exporters roughly grade and ship their lots according to solubility and color, conforming to the requirements of the country of destination. In most cases, the exporters do not bulk the many small lots into large lots, but simply select a number of cans according to the specifications of the consumers abroad.

The United States buys insoluble copaiba chiefly, and pays little attention to the color. Great Britain insists upon light or amber colored, soluble copaiba. Japan and Germany, before the last war, bought both the soluble and insoluble product.

Exports of Balsam Copaiba from Brazil.—According to a report of the United States Department of Commerce, Office of International Trade,[3] Washington, D. C., Brazil exported the following quantities of balsam copaiba during the years following World War II:

Year	*Metric Tons*
1946.....	81
1947.....	94
1948.....	47

Physicochemical Properties of the Oleoresin.—Copaiba balsam is a pale-yellow to yellowish-brown, more or less viscous liquid, some lots exhibiting a slight greenish fluorescence. It possesses a peculiar, aromatic odor. On exposure to air, the oleoresin acquires a dark brown color, a more viscous

(*Top*) Production of cananga oil in the Bantam region of Java (Indonesia). Primitive direct fire stills serve for the distillation of the flowers. (*Bottom*) Cananga oil, Bantam region View of primitive condensers and oil separators. *Photos Fritzsche Brothers, Inc., New York.*

Digitized

(*Top*) Production of ylang ylang oil in Nossi-Bé (Madagascar). A branch of an ylang ylang tree bearing flowers. (*Left*) Native girls with harvested ylang ylang flowers in baskets (Nossi-Bé). (*Bottom*) A large ylang ylang distillery in Nossi-Bé. Native girls carrying the harvested flowers to the distillery in the morning. *Photos Fritzsche Brothers, Inc., New York.*

and partly by polymerization of the essential oil. On aging of the oleoresin, the resinous, nonvolatile portion increases.

Four samples of genuine copaiba balsam collected by the author during a visit to the Amazon Basin had the following properties:

	Insoluble	*Soluble*	*Dark*	*Pale*
Specific Gravity at 25°/25°	0.973	0.962	0.961	0.975
Optical Rotation	−21° 20′	−20° 20′	−20° 18′	−25° 20′
Refractive Index at 20°	1.5117	1.5099	1.5101	1.5118
Acid Number	74.2	67.2	67.1	79.8
Saponification Number	81.2	71.9	73.7	86.8
Evaporation Residue	61.1%	50.0%	49.7%	58.9%
Color	Brown with greenish fluorescence	Reddish-brown	Reddish-brown	Yellow with greenish fluorescence

Freise [4] examined samples of copaiba from the eight most important species of *Copaifera*, viz., *reticulata, guianensis, multijuga, officinalis, martii* var. *rigida, coriacea, martii* Hayne, and *glycycarpa*, and observed considerable variations even in samples from the same species. The range of properties determined by Freise was:

Specific Gravity at 15°/4°	0.888 to 1.004
Optical Rotation at 20°	−14° 45′ to −37° 10′
Acid Number	48 to 86
Saponification Number	44 to 92
Essential Oil Content	26 to 63%

Numerous lots of copaiba balsam imported by Fritzsche Brothers, Inc., New York, from the States of Pará and Amazonas in Brazil had properties varying within these limits:

Specific Gravity at 25°/25°	0.922 to 0.982
Optical Rotation	+20° 0′ to −23° 0′
Refractive Index at 20°	1.5022 to 1.5122
Acid Number	20 to 72.1
Saponification Number	33.6 to 87.5
Evaporation Residue	27.1 to 55.6%

The wide varieties in these properties, particularly in regard to the optical rotation, must be explained by the fact that each can received from Brazil represented a lot originating from a different region, as was explained above. Every lot was tested for adulteration with gurjun balsam and with African copaiba, but none gave a positive reaction.

In general it can be said that copaiba balsam with a high specific gravity and high evaporation residue is preferable for employment as a fixative for

soap perfumes; this type of copaiba possesses a smoother and more lasting odor than copaiba with a low specific gravity and a low evaporation residue. The latter contains more volatile oil and, therefore, lends itself better to distillation purposes.

Adulteration of the Balsam.—Copaiba balsam is occasionally adulterated with fatty oils, turpentine oil, kerosene, or rosin.

As regards rosin, the reader will find a test for its detection in Vol. I of this work, p. 334. It should be pointed out, however, that an infallible test for rosin has not yet been developed.

A test for kerosene and mineral oils in general is described in Vol. I of this work, p. 332 (Oleum Test). Another test for paraffin oils in copaiba balsam is given in the National Formulary.

The National Formulary also describes a test for the presence of turpentine or fatty oils. On evaporation of an accurately weighed sample of

lucent, greenish-brown, almost odorless and tasteless. Relatively little is known about its composition except that it contains several resinoic acids. Most probably the resinous matter is the result of oxidation and polymerization of the oil in the plant cells. The higher its content of oil, the less resinous substances the copaiba contains.

Oil of Copaiba

For the industrial isolation of the volatile oil from the oleoresin, the so-called Pará copaiba (from the Brazilian States of Pará and Amazonas) is preferable to the product from Maracaibo (Venezuela) because the former contains up to 85 per cent of volatile oil. The Maracaibo product (which originates from *Copaifera officinalis*) is more viscous and, upon distillation, yields only 35 to 58 per cent of volatile oil.

Physicochemical Properties of the Oil.—Oil of balsam copaiba is a colorless, yellowish, or slightly bluish liquid possessing a somewhat peppery and aromatic odor, characteristic of the oleoresin itself. Oils distilled from copaiba balsams of different origin exhibit widely varying physicochemical properties, particularly in regard to the optical rotation. Gildemeister and Hoffmann [5] reported properties for several types of oil; we shall quote only those of oils which are of commercial importance today.

	Oils from Pará Copaiba	*Oils from Mandos Copaiba*	*Oils from Maracaibo Copaiba*
Specific Gravity at 15°	0.886 to 0.910	0.9036 to 0.9095	0.900 to 0.905
Optical Rotation	−7° 0′ to −33° 0′	−16° 4′ to −32° 28′	−2° 30′ to −14° 0′
Refractive Index at 20°	1.493 to 1.502	1.50045 to 1.53012	About 1.498
Acid Number	0 to 1.9	0.3 to 0.6	0.9 to 1.0
Ester Number	0 to 4 (in 1 case 13)	0.9 to 6.4	1 to 1.6
Solubility in 95% Alcohol	Soluble in 5 to 6 vol.	Soluble in 6 vol.	Soluble in 5 to 6 vol.

Oils distilled by Fritzsche Brothers, Inc., New York, from imported Pará and Amazonas copaiba had properties varying within these limits:

Specific Gravity at 15°/15°	0.901 to 0.907
Optical Rotation	−10° 30′ to −14° 22′
Refractive Index at 20°	1.4958 to 1.4990
Saponification Number	Up to 1.5

Chemical Composition of the Oil.—The early investigations on the chemical composition of oil of copaiba balsam, carried out by Blanchet,[6] Sou-

[5] "Die Ätherischen Öle," 3d Ed., Vol. II, 864.
[6] *Liebigs Ann.* **7** (1833), 156.

Digitized by Google Original from CORNELL UNIVERSITY

beiran and Capitaine,[7] Posselt,[8] Strauss,[9] Brix,[10] and Levy and Englaender,[11] require no discussion here, because they did not lead to any conclusive results. It was only in 1892 that Wallach [12] succeeded in identifying caryophyllene as the chief constituent of the volatile oil derived from copaiba balsam. Since then, the presence of the following compounds has been reported in the oil:

α- and β-Caryophyllene. Treating the fraction b. 250°–270° with sulfuric acid and glacial acetic acid, Wallach [13] obtained caryophyllene hydrate m. 96°. He arrived at the conclusion that caryophyllene, which also occurs in oil of clove, is the principal constituent of copaiba balsam oil. In 1910, Deussen and Hahn [14] prepared the nitrosochloride and the nitrosate of caryophyllene from copaiba balsam oil, and declared the optically inactive modification of this sesquiterpene to be α-caryophyllene. Schimmel & Co.[15] found that the oil also contains optically active β-caryophyllene, an observation later confirmed by Deussen and Eger,[16] who identified β-caryophyllene in copaiba balsam oils of various origin. (Regarding caryophyllene, see Vol. II of this work, p. 99).

l-Cadinene. In their investigation of copaiba balsam oil, Schimmel & Co.[17] also obtained a dihydrochloride m. 113°–115°, identical with *l*-cadinene dihydrochloride. This led Schimmel & Co. to the conclusion that *l*-cadinene is a constituent of the oil.

Other Sesquiterpenes(?). The same workers also expressed the opinion that copaiba balsam oil contains still other sesquiterpenes, which were not identified, however.

Examining an oil derived from Surinam copaiba balsam, van Itallie and Nieuwland [18] noted the presence of *l-cadinene* or of another sesquiterpene yielding *l*-cadinene dihydrochloride m. 116°–117°, $[\alpha]_D$ −36° 5′ (in chloroform solution). In addition, they isolated a *sesquiterpene alcohol* $C_{15}H_{26}O$, m. 113°–115° which, on dehydration with formic acid, gave a sesquiterpene b_{759} 252°, d_{15} 0.952, α_D −61° 42′, n_D^{15} 1.5189. Van Itallie and Nieuwland did not succeed in identifying caryophyllene, but expressed the opinion that their oil contained other sesquiterpenes, aside from the *l*-cadinene mentioned above.

[7] *Ibid.* **34** (1840), 321.
[8] *Ibid.* **69** (1849), 67.
[9] *Ibid.* **148** (1868), 148.
[10] *Monatsh.* **2** (1881), 507. Cf. Umney, *Pharm. J.* [3], **24** (1893), 215.
[11] *Liebigs Ann.* **242** (1887), 189. *Ber.* **18** (1885), 3206, 3209.
[12] *Liebigs Ann.* **271** (1892), 294.
[13] *Ibid.*

Use.—Copaiba was once used quite extensively in all kinds of medicinal preparations, internal as well as external. Today it is employed chiefly as an odor fixative in the scenting of soaps and technical preparations. It blends well with the ionones and with oil of cedarwood.

The volatile oil derived from the oleoresin is a good diluent of low-priced perfume compositions; its soft odor has a tendency to mellow and harmonize harsh notes of synthetic aromatics.

Suggested Additional Literature

F. W. Freise, "Certain Clarifications Respecting Brazilian Copaiba Balsam," *Süddeut. Apoth. Ztg.* **77** (1937), 11. *Chem. Abstracts* **31** (1937), 2351.

O. R. Gottlieb and A. Iachan, "Study of Copaiba Balsam," *Rev. quim. ind. Rio de Janeiro* **14**, No. 163 (1945), 20. *Chem. Abstracts* **40** (1946), 5207.

OIL OF BALSAM COPAIBA AFRICAN

The African copaiba balsam, also known as Illurin balsam, originates from Nigeria and adjacent parts of West Africa. According to Umney,[1] Solereder,[2] and Engler and Prantl,[3] the tree which produces the oleoresin, is probably *Oxystigma mannii* Harms (*Hardwickia*(?) *mannii* Oliv.), fam. *Leguminosae*. African copaiba balsam, which was once handled via the London market, is now rarely met with, and few, if any, commercial lots are encountered.

Physicochemical Properties of the Oil.—On steam distillation, the oleoresin yields from 37 to 57 per cent of volatile oil, for which Gildemeister and Hoffmann,[4] reported these properties:

Specific Gravity at 15°	0.917 to 0.930
Optical Rotation	+5° 45′ to +39° 0′
Refractive Index at 20°	1.50574 to 1.50811
Acid Number	0.5 to 9.3
Ester Number	0 to 5.6
Ester Number after Acetylation (One Determination)	10

[1] *Pharm. J.* [3], **22** (1891), 449; **24** (1893), 215.
[2] *Arch. Pharm.* **246** (1908), 72.
[3] "Die natürlichen Pflanzenfamilien," Suppl. to the 2nd to 4th Parts (1897), 195.
[4] "Die Ätherischen Öle," 3d Ed., Vol. II, 870.

Digitized by Google
Original from CORNELL UNIVERSITY

Solubility..... Soluble in 98% alcohol; slightly opalescent on addition of 2 and more vol. Soluble in 10 vol. of 95% alcohol with opalescence

Chemical Composition of the Oil.—The following compounds have been reported in the volatile oil derived from African copaiba balsam:

β-Caryophyllene. Very small quantities (less than 1 per cent) were found in the lowest boiling fraction b_{15} 128°–129.5° by Deussen [6] and Schimmel & Co.[6]

d- and *l*-Cadinene. The last-named authors [7] also noted that the fraction b. ~240° consists chiefly of *d*-cadinene $[\alpha]_D$ +60° 40′. As regards the *l*-cadinene, it was identified by von Soden,[8] and Schimmel & Co.[9]

Copaene. Investigating the fraction b. 246°–251°, Schimmel & Co.[10] noted the presence of a sesquiterpene $[\alpha]_D$ −13° 21′, which yielded a dihydrochloride m. 117.5°–118° identical with that of *l*-cadinene. Shortly afterward, however, Semmler and Stenzel [11] determined that the sesquiterpene in question was not *l*-cadinene, but copaene (cf. Vol. II of this work, p. 122).

Use.—The oil derived from African copaiba balsam was at one time used as an occasional adulterant of the oil from Brazalian copaiba balsam.

OIL OF BALSAM PERU

Essence de Baume de Pérou *Perubalsamöl*
Aceite Esencial Balsamo Peru *Oleum Balsami Peruviani*

BALSAM PERU

History.—The designation "Balsam Peru" is misleading, inasmuch as it implies that the balsam originates from Peru, whereas in reality it is produced chiefly in El Salvador. The misnomer dates from early colonial days, when products from the Pacific coast of Spanish America were assembled in Callao, Peru, shipped to Panama, transported across the Isthmus, and transshipped to Europe. In those days balsam was transported by land from Salvador across the Isthmus and loaded into ships carrying Peruvian

[5] *Liebigs Ann.* **388** (1912), 142.
[6] *Ber. Schimmel & Co.*, April (1914), 44.
[7] *Ibid.*
[8] *Chem. Ztg.* **33** (1909), 428.
[9] *Ber. Schimmel & Co.*, October (1909), 31.
[10] *Ibid.*, April (1914), 44.
[11] *Ber.* **47** (1914), 2555.

Digitized by Google Original from CORNELL UNIVERSITY

thirds of that during the dry season. In the flowering season (April) the trees also seem to yield less balsam than at other times.

Production of Peru Balsam.—Two processes are in use today:

1. The so-called *cascara* or "bark process." Here (as well as in the other process described below), the tree must first be scorched by making a fire at its base. After ten minutes of scorching, the tree is left standing for about eight days, when the bark becomes so soft that pieces 1 to 2 ft. long and about 1 ft. wide can be cut out with a machete. Subsequent incisions are made either on the opposite side of the tree or above the first incision so that the tree will not be damaged too much. If made one above the other, the incisions become longer and longer. Supported by ropes and pulleys, the workers then climb high up—quite a dangerous task—and scorch the tree with torches.

The removed bark is crushed and subsequently pressed in primitive presses sheltered beneath a shed, hot water being poured over the bark several times, to soften the balsam and facilitate its flow. After the liquid is cooled, the balsam, which is heavier than water, settles at the bottom of the container and can be separated. The supernatant layer of water contains only very little balsam.

2. The so-called *pañal* (cloth) or *trapo* process. This is simply a continuation of the *cascara* process. After the bark has been removed by incisions, burlap is calked into the incisions to absorb the balsam exuding from the wound. After eight or ten days, these pieces of burlap are saturated with balsam and can be removed. They are boiled in water for about 1 hr., and subsequently pressed in the above-described presses, which also serve for the bark. The balsam separates on the bottom of the container and can easily be obtained by drawing off the water.

The *trapo* process yields about two to four times as much balsam as the *cascara* process, because new incisions for obtaining new pieces of bark should be made only every two months, while the same incisions can be treated every two weeks by the *trapo* process as long as the trees are in full vigor, i.e., from forty to sixty or more years old. However, it is advisable to treat one incision only twice and then make a new incision above the previous one, or on the opposite side of the trunk.

Thus it appears that an average yield of balsam is 4 to 6 oz. with each extraction. Assuming that a tree is tapped twenty-four times a year, the total yearly yield would be from 96 to 144 oz. per tree. However, during the rainy season the tree "cools off," and the tapping cannot be done twice a month. Eighteen tappings per year per tree would be a safe estimate.

Purification of the Balsam.—After separation from the aqueous layer, the balsam is purified by boiling for 2 or 3 hr. above an open fire. This causes the water still present in the balsam to evaporate. Scum, dirt particles, and impurities are skimmed off, and the product is strained while still hot. The final balsam must flow clear and easily.

Obviously, the heating of the balsam with open fire is a rather crude practice, and has some deteriorative effect upon the odor of the final product, the more volatile constituents being driven off. Purification by more advanced methods produces a balsam superior to that regularly shipped from El Salvador—as has been proved in the laboratory. Unfortunately, competition in balsam Peru is so keen that the article can scarcely stand the added expense of purification outside of the country of origin.

Twenty pounds of balsam obtained by the *cascara* process are usually mixed with about one hundred pounds of *trapo* balsam. Since thinner, more liquid balsam is considered to be of higher quality than thick balsam, the *trapo* product is preferred to the *cascara;* the former has a lower specific gravity and a higher oil content.

Economic Set-up.—The trees are generally owned by landed proprietors who, during periods of low balsam prices, share the cost of production with the peons on an equal basis, all actual working expenses being carried by the peons. The lots produced on the various estates are sold, usually through middlemen, to exporters in San Salvador.

Exports of Balsam Peru from El Salvador.—According to a report of the United States Department of Commerce, Office of International Trade,[2] Washington, D. C., the total exports of balsam Peru prior to 1940 varied

in ether and in petroleum ether. Shipments of genuine Peru balsam from El Salvador examined by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 25°/25°	1.152 to 1.170
Acid Number	56.2 to 83.0
"Cinnamein" Content	47.0 to 58.7%, seldom below 50%
Saponification Number of the "Cinnamein"	230.5 to 240.0
Solubility	Soluble in high-proof alcohol, chloroform and glacial acetic acid, with not more than opalescence. Only partly soluble in ether and petroleum ether

Bennett [3] reported these properties for Peru balsam:

Specific Gravity at 15.5°	1.140 to 1.160
Refractive Index at 25°	1.588 to 1.595
Refractive Index at 25° of the extracted "Cinnamein"	1.575 to 1.582
Solubility	Not clearly soluble in 90% alcohol, a flocculent, waxy precipitation finally settling out on standing

Numerous papers have been published on various methods of assaying the balsam, but the scope of the present work does not permit their discussion, particularly in view of the fact that many of these methods have little, if any, value. Suffice it to refer the reader to the official tests of the United States Pharmacopoeia. The "cinnamein" content (see below) is determined by extraction with ether. It ranges from 50 to 60 per cent by weight, calculated upon the original balsam. In balsams of good quality, the "cinnamein" content should not be below 50 per cent. The analysis of Peru balsam also includes determination of the saponification number of the extracted "cinnamein," which should range from 230 to 240.

Occasionally Peru balsam is adulterated with rosin. A test for the detection of rosin will be found in Vol. I of the present work, p. 334. It should be pointed out, however, that an infallible rosin test has not yet been developed.

Other adulterants of Peru balsam are fatty oils and all kinds of low-priced gums. The rigid specifications of the United States Pharmacopoeia,

sam to any chemical tests because the price of the product does not warrant analysis in special test laboratories. The exporters simply examine the balsam according to color, transparency, and flow, and whenever necessary a lot is reworked and purified by boiling it over an open fire, and eliminating moisture and mechanical impurities.

Chemical Composition of the Balsam.—Peru balsam is a complex mixture consisting of about 25 to 30 per cent of resin and 60 to 65 per cent of essential oil [4] (see below). The resinous part of the balsam is composed chiefly of an alcohol, viz., peru-resinotannol, which occurs in the balsam partly free, and partly esterified with cinnamic acid and benzoic acid.

Oil of Balsam Peru

Extraction of the Oil.—The oil of balsam Peru, in commerce at one time referred to as "cinnamein," possesses such a high boiling point that it cannot be isolated from the balsam by steam distillation. In technical practice the oil is, therefore, extracted from the balsam by means of volatile solvents such as petroleum ether or benzene, after neutralization of the free acids. The yield of oil in commercial production ranges from about 43 to 55 per cent, the average being about 50 per cent.

Physicochemical Properties of the Oil.—Oil of balsam Peru is a reddish-brown, slightly viscous liquid, possessing a pleasant, warm, balsamic, sweet and lasting odor. Gildemeister and Hoffmann [5] reported these properties for the oil:

Specific Gravity at 15°	1.102 to 1.122
Optical Rotation	Slightly dextrorotatory up to +2° 30′
Refractive Index at 20°	1.570 to 1.580
Acid Number	24 to 52
Ester Number	200 to 250
Solubility	Miscible with 90% alcohol in any proportion; sometimes soluble up to 1 vol. of 90% alcohol. On dilution the solution exhibits slight opalescence either immediately or after standing

Numerous lots of oil isolated by Fritzsche Brothers, Inc., New York, from pure Peru balsam (origin El Salvador) had properties varying within the following limits:

Specific Gravity at 15°/15°	1.102 to 1.110

Saponification Number..... 246.5 to 267.9
Solubility..... Soluble in 0.5 vol. of 90% alcohol and more

Chemical Composition of the Oil.—Oil of balsam Peru consists chiefly of "cinnamein," the latter being largely a mixture of esters in which benzyl benzoate and benzyl cinnamate predominate. The proportions of these esters appear to vary in oils derived from balsam of different origin. The following compounds have been reported in the oil:

Benzyl Benzoate. An oil examined by Tschirch and Trog [6] consisted chiefly of benzyl benzoate.

Benzyl Cinnamate. On the other hand, in several oils investigated by Thoms,[7] benzyl cinnamate appeared to predominate.

Peruviol(?). The same author also reported the presence of an alcohol $C_{13}H_{22}O$, b_7 139°–140°, $d_{17.5}$ 0.886, α_D +13° 0′, esterified probably with a dihydrobenzoic acid. The freed alcohol exhibited a pleasant odor, reminiscent of honey and narcissus.

d-Nerolidol. A more thorough investigation of peruviol by Schimmel & Co.,[8] however, showed that this alcohol consists to the greater part, if not entirely, of nerolidol (cf. Vol. II of this work, p. 260).

Farnesol. Reported as constituent of Peru balsam oil by Elze.[9]

Vanillin. Identified by Schmidt.[10]

Cinnamyl Alcohol(?). Delafontaine [11] expressed the opinion that cinnamyl alcohol occurs in oil of balsam Peru, but according to Gildemeister and Hoffmann [12] this is probably not the case.

Cinnamyl Cinnamate. The presence of this ester in oil of balsam Peru has been reported in literature.[13] However, no experimental data have been presented to this effect.

Stilbene(?). Also reported many years ago by Kachler,[14] but presence unlikely (Gildemeister and Hoffmann).

The fact that the above-mentioned compounds occur in the balsam (which is a pathological exudate of the tree) raises the question whether all of them are pathological products of the tree. This problem was recently studied by Naves [15] who examined wood of *Myroxylon pereirae* Klotzsch,

[6] *Arch. Pharm.* **232** (1894), 70.
[8] *Ber. Schimmel & Co.*, April (1914), 75.

imported from the province of Sonsonato in El Salvador. One log was derived from a healthy tree, the other from a tree that had been used for the production of balsam. Examination under the microscope showed that the brown heartwood is surrounded by a wide whitish zone, viz., the sapwood. The oil glands in the heartwood are impregnated with essential oil, whereas those in the sapwood are empty. The sapwood, whether of healthy trees or of trees used for the production of balsam, contains very little essential oil. The oil is localized in the heartwood.

Distilling the wood of the healthy and that of the wounded tree, Naves obtained 0.736 and 1.08 per cent, respectively, of essential oil. The two types of oil had the following composition:

	From Healthy Trees (%)	*From Wounded Trees* (%)
Cadinenes	28 to 30	6 to 8
l-Nerolidol, free	50 to 52	68 to 70
l-Cadinol, free	12 to 14	7 to 9
Alcohols, esterified	About 2	About 6

Thus the wood of the healthy tree yielded less essential oil and much less nerolidol than the wood of the tree used for the production of balsam. As a result of his observations, Naves suggested that the wood of trees exhausted of balsam be used in Salvador for recovery of its oil by distillation. The essential oil thus obtained is very rich in *d*-nerolidol, a highly esteemed perfume material that imparts "sleekness" and smooth tonalities to otherwise harsh compositions.

Continuing his work, Naves [16] also investigated the essential oil derived from the *fruit* of *Myroxylon pereirae* Klotzsch and found that it contains a laevorotatory bicyclic sesquiterpene. On treatment with gaseous hydrogen chloride, this sesquiterpene yielded *l*-cadinene dihydrochloride; on hydrogenation the sesquiterpene gave a hydrocarbon which appeared to be *trans*-tetrahydrocadinene. The sesquiterpene was accompanied by an isomer that readily oxidized or polymerized, and by a small quantity of sesquiterpene alcohols.

More recently Naves and Ardizio [17] found that the oil derived from the

of Peru, a very viscous, dark brown mass of pleasant odor and high fixation value. According to Naves and Mazuyer,[18] the yield of resinoid on extraction with benzene varies between 80 and 86 per cent.

Naves and Mazuyer reported the following properties for resinoids of Peru, obtained by extraction with alcohol (I), and by extraction with benzene (II):

	I	*II*
Specific Gravity at 15°	1.140 to 1.170	1.103 to 1.126
Optical Rotation	Up to +2° 20′	Up to +2° 44′
Refractive Index at 20°	1.590 to 1.599	1.568 to 1.582
Acid Number	55 to 84	22.4 to 48.6
Ester Number	168 to 220	198 to 260

The resinoid prepared by extraction with alcohol offers the advantage of solubility in high-proof alcohol and a very lasting odor.

Use.—Peru balsam is used mainly in pharmaceutical preparations—dressing of wounds, e.g. The oil and the resinoid are employed chiefly in perfumes, soaps and cosmetics (see the monograph on "Oil of Balsam Tolu").

OIL OF BALSAM TOLU

Essence de Baume de Tolu *Tolubalsamöl*
Aceite Esencial Balsamo Tolu *Oleum Balsami Tolutani*

Balsam Tolu

Botany and Origin.—The taxonomy of the tree from which balsam Tolu is derived has been the subject of considerable controversy. Official standard works (United States Pharmacopoeia and British Pharmacopoeia) now classify the tree as *Myroxylon balsamum* (L.) Harms (fam. *Leguminosae*). Tschirch [1] expressed the belief that the trees yielding balsam Tolu and balsam Peru 'are merely physiological forms of *Toluifera balsamum* L. Harms [2] stated that balsam Tolu is derived from *Myroxylon balsamum* (L.) Harms var. *α genuinum* Baill., and balsam Peru from *Myroxylon balsamum* (L.) Harms var. *β pereirae* (Royle) Baill.

[18] "Les Parfums Naturels," Paris (1939), 295.
[1] "Die Harze und Harzbehälter," Vol. 2, 2d Ed. (1906), 1204, 1208.
[2] *Notizbl. bot. Gart. Berlin-Dahlem* **5** (1908), 95.

Digitized by Google Original from CORNELL UNIVERSITY

Myroxylon balsamum L., a tall tree with a spreading crown, differs from the Peru balsam tree only by its habit of branching about 15 m. aboveground. It occurs wild in the great forests of the province Tolu, along the Magdalena and Cauca rivers in Colombia. The balsam forms in trunk tissues as the result of injuries. To stimulate the formation of balsam, Indians lacerate the bark of the trunk by making deep V-shaped incisions with machetes. The balsam is collected in small cups, which are inserted in slight excavations beneath the point of the two vertical incisions meeting at the lower end. As many as twenty cups have been observed at a time on one tree. The workers go from tree to tree, emptying the cups into bags of rawhide slung over the back of a donkey. In these skin vessels the product is then brought to the shipping ports.[3] Collection of the balsam continues all year around, except for the period of heavy rains, when the forests become impassable. The balsam is packed in tin cans and exported mainly from Barranquilla.

Total exports of balsam Tolu per year amount to about 80,000 kg. net.

There exists only one quality of balsam Tolu; various lots differ merely in color, which ranges from light yellow to reddish black. No price differential is made because of color.

Physicochemical Properties of the Balsam.—Tolu balsam is a brown or yellowish-brown, semisolid or plastic mass with a pleasant, aromatic, lasting and sweet odor, reminiscent of vanilla. The consistency of the balsam depends upon its age and the temperature. On standing, it turns into a plastic solid, softening at about 30° and melting between 60° and 65°. With age the balsam becomes brittle. Tolu balsam is soluble in 95 per cent alcohol, in ether, and in chloroform, but nearly insoluble in petroleum

remove all such foreign material, and the presence of minute amounts does not violate the usual standards set up in the United States.[4]

Many cans of Tolu balsam contain small quantities of water which rise to the top and should be taken into consideration when drawing a sample of balsam for analysis. Standards and tests are described in the United States Pharmacopoeia. Balsam Tolu is occasionally adulterated with rosin. A test for the detection of rosin in Tolu balsam will be found in Vol. I of the present work, p. 334. It should be mentioned, however, that an infallible rosin test has not yet been developed. Much work has been done on the analysis of Tolu balsam, particularly by van Itallie and his collaborators,[5] by Rosenthaler,[6] and Bennett.[7] For details the reader is referred to the original literature.

The chemical composition of Tolu balsam is complex with the result that the literature contains contradictory statements on the subject.[8] To summarize investigations covering a period of more than fifty years: the balsam, like Peru balsam, appears to contain a mixture of resinous substances, benzyl benzoate, some benzyl cinnamate, a small percentage of essential oil, and traces of vanillin. The proportion of resinous matter is larger than in Peru balsam, amounting to 75 or 80 per cent. On saponification, the chief constituent of Tolu balsam, the so-called "tolu-resin," yields an alcohol —viz., tolu-resinotannol—and cinnamic and benzoic acids. The "tolu-resin" is easily soluble in 95 per cent alcohol, acetone, or glacial acetic acid, insoluble in petroleum ether. (Petroleum ether dissolves from 2 to 10 per cent of the balsam; the soluble portions consist of cinnamic and benzoic esters, vanillin, and perhaps some terpenes.[9])

According to the British Pharmacopoeia, 1948 (p. 84), Tolu balsam should contain "not less than 35 per cent., and not more than 50 per cent., of total

sure steam results in oils lighter than water; superheated steam or steam of high pressure gives better yields and oils of higher specific gravity.

Physicochemical Properties of the Oil.—Oil of balsam Tolu is a somewhat viscous liquid with an agreeable, lasting and sweet odor, slightly reminiscent of hyacinth. Gildemeister and Hoffmann [10] reported the following properties for oil of balsam Tolu:

Specific Gravity at 15°	0.945 to 1.09
Optical Rotation	−1° 20′ to +0° 54′
Refractive Index at 20°	1.537 to 1.560
Acid Number	5 to 34
Ester Number	153 to 208
Solubility	Usually not clearly soluble in 80% alcohol. Soluble in 1 vol. of 90% alcohol, opalescent to turbid with more; separation of floccules in the latter case

Oils of balsam Tolu distilled by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.907 to 1.016
Optical Rotation	−1° 5′ to −4° 0′
Refractive Index at 20°	1.5075 to 1.5347
Acid Number	23.8 to 80.0
Saponification Number	85.9 to 171.1
Solubility	Soluble in 0.5 vol. and more of 90% alcohol

Chemical Composition of the Oil.—Early investigations [11] into the chemical composition of the volatile oil derived from balsam Tolu, which were carried out about a century ago, gave only vague and partly contradictory results. They need not be discussed here. The following compounds are probably present in the oil:

Phellandrene(?). In the fraction b. 170° Kopp [12] observed a terpene with an odor reminiscent of elemi gum. It was apparently phellandrene.

Benzyl Benzoate and Benzyl Cinnamate. Years ago Busse [13] identified benzyl benzoate and benzyl cinnamate in the balsam itself. Most probably these esters are present also in the distilled oil, because the oil exhibits a high ester number and, on saponification, yields crystalline acids (apparently benzoic acid and cinnamic acid).

Farnesol. According to Elze,[14] oil of balsam Tolu also contains traces of farnesol. Recently confirmed by Naves [15]

Submitting Tolu balsam to dry distillation, Dupont and Guerlain [16] obtained substantial quantities of benzoic acid and cinnamic acid, as well as guaiacol, creosol, and perhaps 4-hydroxy-3-methoxy-1-ethylbenzene. Carbon dioxide and hydrogen developed during distillation.

In order to compare the chemical composition of the oil derived from balsam Tolu (which is a pathological exudate of the tree) with that of the essential oil contained in the *wood* of a healthy tree, Naves [17] imported two logs of *Myroxylon balsamum* L. from San Juan de Uraba, one of the principal producing regions of Tolu balsam in Colombia. One log came from a healthy tree, the other from a tree which had served for the production of balsam. Naves found that the oil is present chiefly in the red heartwood of the trunk. The wood of the tree that had been wounded contained more oil than the wood of the healthy tree. However, in regard to chemical composition the oils from the two trees were identical. Naves reported the presence of the following compounds in the oil derived from the wood of *Myroxylon balsamum* L.:

l-Cadinol. The chief constituent.

d-Cadinene and Other Sesquiterpenes.

Farnesol. Small quantities.

Nerolidol. Traces (only one-fifteenth of the quantity of farnesol).

Resinoid of Tolu.—On repeated extraction with high-proof alcohol, removal of any impurities present by filtration, concentration of the filtrates (removal of the alcohol), Tolu balsam yields the so-called resinoid of Tolu, a very viscous, dark mass of pleasant odor and high fixation value. According to Naves and Mazuyer,[18] the yield of resinoid varies between 60 and 66 per cent. The resinoid has an acid number ranging from 112 to 154, and an ester number varying between 53 and 72. The resinoid contains from 2.5 to 12 per cent of essential oil. The resinoid offers the advantage of being a clear, viscous, and water-free liquid.

oriental, types of compositions. The oleoresin is an excellent odor fixative, and at the same time imparts warm tonalities to a perfume compound.

Suggested Additional Literature

C. T. Bennett, "Balsam of Tolu," *Perfumery Essential Oil Record* **19** (1928), 464.

OIL OF CABREUVA

Myrocarpus frondosus Fr. Allem. and *Myrocarpus fastigiatus* Fr. Allem. (fam. *Leguminosae*), the so-called "Cabreuva," are tall trees attaining a height of 12 to 15 m. The cabreuva tree grows wild in many parts of southern Brazil (States of São Paulo and Rio de Janeiro), in Paraguay, and northern Argentina.

The wood of these trees is very hard and is used extensively for the construction of houses and ships. In the State of São Paulo, the waste shavings and sawdust are occasionally employed for the extraction of the essential oil. When lacerated by incisions, the trunks of the live trees produce a pathological exudate closely resembling the balsam Peru. Because of this similarity, the balsam of the cabreuva tree has been known for centuries as "Baume du Pérou brun" or "Baume du Pérou rouge en coques."[1] It was described in old European pharmacopoeias, but is now used only by natives in Brazil to heal wounds and ulcers and to obviate scars.

The heartwood of the trees contains an essential oil of pleasant odor, which can be isolated by steam distillation. It was distilled experimentally for the first time many years ago by Peckolt.[2] Lately substantial quantities of the so-called cabreuva oil have been produced commercially, particularly in the State of São Paulo. According to information gathered by the author in the producing regions, the distillation of 700 kg. of shavings

A genuine oil produced under the author's supervision in Mattão, São Paulo, had these properties:

Specific Gravity at 15°	0.893
Optical Rotation	+8° 0′
Refractive Index at 20°	1.4845
Acid Number	0
Ester Number	0
Ester Number after Acetylation	144
Boiling Range at 6 mm	124°–138°
Solubility	Soluble in 6 vol. and more of 70% alcohol

An oil of cabreuva examined by Naves [3] exhibited the following properties:

Specific Gravity at 20°/4°	0.8875
Optical Rotation	+8° 20′
Refractive Index at 20°	1.48322
Ester Number	2.2
Alcohol Content, Calculated as $C_{15}H_{26}O$ (Cold Formylation)	82.9%

On fractionation, this oil yielded about 80 per cent of nerolidol.

Chemical Composition.—The chemical composition of cabreuva oil was investigated by Naves [4] who reported the presence of these compounds in the oil:

Tetrahydro-Δ^3-*p*-toluic Aldehyde. Very small quantities only. Identified by oxidation to tetrahydro-Δ^3-*p*-toluic acid m. 99°.

p-Methylacetophenone. Also in very small quantities (cf. Vol. II of this work, p. 476).

l-1-Methyl-4-acetyl-1-cyclohexene (*p*-Methyl-3-tetrahydroacetophenone). In very small quantities only (cf. Vol. II, p. 482).

d-Nerolidol. The chief constituent (about 80 per cent) of the oil. The nerolidol present in cabreuva oil is a mixture of two isomers (cf. Vol. II, p. 260).

Farnesol. Aside from *d*-nerolidol, the oil contains about 2.5 per cent of farnesol (cf. Vol. II, p. 258).

Other Sesquiterpene Alcohols(?). The nerolidol and farnesol are accompanied by a mixture of laevorotatory sesquiterpene alcohols $C_{15}H_{26}O$. One of them is *bisabolol*, another appears to be a bicyclic sesquiterpene alcohol of the cadalene group, and a third one an azulogenic sesquiterpene alcohol.

[3] *Helv. Chim. Acta* **30** (1947), 277.
[4] *Ibid.* **30** (1947), 275, 278; **31** (1948), 44. Cf. *ibid.* **31** (1948), 408; **32** (1949), 2181. *Perfumery Essential Oil Record* **38** (1947), 191; **39** (1948), 280.

Digitized by Google Original from CORNELL UNIVERSITY

A comparison of the chemical composition of cabreuva oil with that of bois de rose oil shows that cabreuva oil may be considered a sesquiterpene homologue of bois de rose oil (Naves):

Cabreuva Oil	*Bois de Rose Oil*
Nerolidol	Linaloöl
Farnesol	Geraniol-Nerol
Bisabolol	Terpineol

Use.—Oil of cabreuva is an excellent odor fixative in perfumes, cosmetics and in the scenting of soaps. The chief use of the oil, however, is as a starting material for the isolation of farnesol (Patent L. Givaudan et Cie., S.A. Geneva, Switzerland).

CONCRETE AND ABSOLUTE OF CASSIE

There are two species of *Acacia* (fam. *Leguminosae*) which have been used for the commercial extraction of their natural flower oils, viz., *Acacia farnesiana* Willd., and *A. cavenia* Hook. et Arn. According to some botanists,[1] the latter is only a variety of the former. Of the two, *Acacia farnesiana* has always been preferred because it yields a flower oil with a much finer odor than that from *Acacia cavenia*. As a matter of fact, the latter is no longer produced in substantial quantities, having been replaced almost entirely by *A. farnesiana*. For the sake of completeness, however, we shall now discuss the two species in order.

I. *Acacia Farnesiana*

Acacia farnesiana Willd., our common sweet acacia, in France called *Cassie ancienne*, is a thorny, much branched shrub, up to 10 ft. in height, and bearing round, yellow-red flower beads in small clusters. It grows spontaneously in many tropical and warm countries. In Southern France, Syria, Egypt, Algeria, and lately in Morocco, it is cultivated for the treat-

once grown extensively, it has repeatedly suffered from attacks by cold weather; therefore plantings here are gradually disappearing, being replaced by those in North Africa. Another reason lies in the development of the French Riviera into a fashionable resort and tourist center; cassie plantations formerly located near Cannes (Le Cannet, Vallauris, Mougins, Saint-Laurent-du-Var) have been parceled off for the building of villas. Labor, too, has become too expensive on the glamorous Côte d'Azur—and the cultivation, particularly the harvesting, of *Acacia farnesiana* requires a great deal of labor. The plant is covered with numerous large thorns, the flowers are hard to reach, and the picking represents a difficult, if not painful, task.

In Southern France, branches of *Acacia farnesiana* are often grafted upon *A. cavenia*, which is a much hardier and frost-resistant plant. Any branches damaged by frost are trimmed off and replaced by new graftings from *A. farnesiana*. Two years after such operation the branches will again bear a normal flower harvest. When in full production, and depending upon its size, a bush yields from 1 to 2, in exceptional cases up to 5, kg. of flowers per year. The harvest begins at the end of September and lasts until the end of December. The flowers are collected twice every week. Toward the end of February the branches are usually pruned, in order to keep the bush within a size that facilitates harvesting of the flowers during the next season.

In Egypt, which now produces substantial quantities of concrete of cassie, conditions for the growth of *Acacia farnesiana* are much more favor-

withstand transplanting without too high mortality. In the first year after transplanting the bushes will develop a few flowers; after the third year a bush will yield from 300 to 1,000 g. of flowers. The buds appear in September, but the harvest does not start before October and lasts until April, with a marked decline of productivity, however, in December and January. In April the branches are pruned (while they still contain some flowers) in order to keep the bushes within a size that allows the children to reach all flowers by hand. Four to six weeks after pruning the branches again attain a length of 1 m. For this reason the trimming has to be done quite closely, particularly after the fourth year, when the bushes have attained full growth.

As regards production in France, about 35 metric tons of flowers were processed in 1900. Since then the quantity has declined steadily and at present amounts to only 2 metric tons per year. Egypt and Algeria each produce 3 or 4 tons of flowers every year for extraction purposes. Morocco has only recently started to develop plantations of *Acacia farnesiana,* and substantial quantities of flowers may be expected in the future.

In the author's experience, about 200 to 250 kg. of *Acacia farnesiana* flowers are required to yield 1 kg. of concrete. According to Naves and Mazuyer,[2] the yield of concrete usually varies within 0.50 and 0.70 per cent, but may be as high as 0.82 per cent, in exceptional cases. The flowers collected at the end of the season (late spring) in general give a higher yield of concrete than those gathered in the fall.

Physicochemical Properties.—Concrete of *Cassie ancienne* is a solid,

On treatment with high-proof alcohol in the usual way, concrete of *Cassie ancienne* yields from 30 to 35 per cent of alcohol-soluble absolute.

An absolute of *Cassie ancienne* from Grasse (I), described by Naves and Mazuyer,[5] and absolutes from Liguria, Italy (II), prepared by Rovesti,[6] had the following properties:

	I	*II*
Specific Gravity at 15°	0.988	1.020 to 1.070
Optical Rotation	...	0° up to −3° 0′
Refractive Index	...	1.514 to 1.521
Acid Number	62.8	18 to 55
Ester Number	33.5	97 to 243

Chemical Composition.—About fifty years ago the chemists of Schimmel & Co.[7] investigated an absolute of maceration which they had obtained by treating 115 kg. of cassie pomade from India three times with alcohol. Concentration of the alcoholic washings and steam distillation of the residual absolute yielded 315 g. of a dark oil which, on rectification with steam, gave 197 g. of oil; d_{15} 1.0475, α_D ±0°, n_D^{20} 1.51331, sap. no. 176. Schimmel & Co. reported the presence of the following compounds in the volatile oil thus obtained:

Benzaldehyde. Semicarbazone m. 214°.

Anisaldehyde. Oxidation to anisic acid m. 180°.

Decylaldehyde. Semicarbazone m. 97°.

Cuminaldehyde. Semicarbazone m. 200°.

A Ketone(?). With a menthone-like odor; b. 200°–205°, d_{15} 0.9327, α_D −3° 50′; semicarbazone m. 177°–178°.

A Ketone(?). With a violet-like odor; b_{15} 133°; *p*-bromophenylhydrazone m. 103°–107°. This ketone appears to be very important for the odor of the cassie flower oil.

p-Cresol. Small quantities.

Methyl Salicylate. The oil obtained by Schimmel & Co. from the Indian pomade contained 11 per cent of methyl salicylate. A wax-free extract of *Cassie ancienne* examined by von Soden [8] contained 30.9 per cent of esters, calculated as methyl salicylate.

Benzyl Alcohol. Identified by means of the phenylurethane m. 177°, and of the acid phthalic ester m. 105°–106°.

[5] "Les Parfums Naturels," Paris (1939), 198.

Geraniol(?) and Linaloöl(?). Presence probable, but not definitely established by Schimmel & Co.

Farnesol. Reported in the high boiling constituents by Haarmann and Reimer.[9]

More recently, La Face [10] investigated an absolute of *Acacia farnesiana* (prepared from a genuine Calabrian concrete; yield of absolute 36 per cent), and found that the absolute contained no eugenol and no methyl salicylate —important constituents of the natural flower oil derived from Roman cassie (*Acacia cavenia*—see below).

La Face proved the presence of the following compounds in the natural flower oil obtained by volatile solvent extraction of *Acacia farnesiana:*

Benzyl Alcohol.

Linaloöl.

α-Terpineol.

Nerolidol or Farnesol (or both), partly esterified.

A Mixture of Cresols.

A Mixture of Ethyl Phenols.

Hydroxyacetophenone.

A Ketone with an ionone configuration (probably optically active α-ionone).

Coumarin.

Butyric Acid.

Palmitic Acid, free (about 50 per cent of the free acids present in the absolute).

Benzoic Acid.

Salicylic Acid.

n-Eicosane.

According to La Face, the perfume of the absolute is due chiefly to the odor complex cresol, ethyl phenol, and coumarin.

Use.—Absolute of *Cassie ancienne* is a valuable adjunct in the creation of high-grade perfumes of the French type. It imparts elegant notes to floral as well as oriental scents. The absolute has to be dosed carefully and well blended in order to obtain the desired effects. It harmonizes particularly well with violet, orris, and the ionones.

[9] German Patent No. 149,603 (1902). Cf. *Chem. Zentr.* (1904), I, 975.
[10] *Helv. Chim. Acta* **33** (1950), 249.

Digitized by Google Original from CORNELL UNIVERSITY

II. *Acacia Cavenia*

Acacia cavenia Hook. et Arn. is a large shrub with stout spines, often grown in hedges. It was introduced into Southern France from Italy; hence the name "Roman cassie" or *Cassie romaine.* The flowers resemble those of *Acacia farnesiana,* but their perfume is somewhat harsher, more spicy, and less pleasing than that of the flowers from *Acacia farnesiana.* For this reason, perfumers prefer the latter, and, when buying cassie flowers, the manufacturers in Grasse attempt to obtain only those of *Acacia farnesiana.* This, however, is not always possible and for a long time it has been the practice of the growers to supply a mixture of two parts of *Acacia farnesiana* and one part of *Acacia cavenia.* The price of the former has usually been about twice that of the latter. Because of the development of real estate in the vicinity of Cannes, the plantations of *Cassie romaine* are now gradually disappearing, and it will not be long before flowers from this plant are no longer available. The manufacturers in Grasse do not regret this development. In general, *Acacia cavenia* is a hardier plant than *Acacia farnesiana* and does not suffer so much from attacks by frost and drought. It requires much less care than *Acacia farnesiana.* The flowers appear in September and can be harvested up to May. There is a lull in December and January, and a new bloom in spring.

Formerly the natural perfume was isolated from the flowers by means of maceration with hot fat (cf. Vol. I of this work, p. 198), but this process has been gradually replaced by extraction with petroleum ether.

According to the author's experience, about 200 kg. of flowers are required to yield 1 kg. of concrete. Naves and Mazuyer [11] reported yields

	I	*II*
Specific Gravity at 15°	1.031	1.028
Optical Rotation	±0°	+0° 14′
Refractive Index at 20°	1.5120	1.5140
Acid Number	11.2	22.0
Ester Number	96.0	112.0

On treatment with high-proof alcohol, in the usual way, the concrete yields from 30 to 35 per cent of an alcohol-soluble absolute. An absolute of *Cassie romaine* of French origin was examined by Naves and Mazuyer: [14]

Specific Gravity at 15°	0.984
Optical Rotation	+8° 20′
Refractive Index at 20°	1.5037
Acid Number	33.6
Ester Number	49

Chemical Composition.—Walbaum [15] investigated a steam-volatile oil of *Acacia cavenia* which he had obtained by steam distillation of a petroleum ether concrete. Treatment of two samples with dilute sodium hydroxide solution gave these portions:

	Per Cent	*Per Cent*
Phenolic Constituents	5.5	3
Nonphenolic Constituents	8.8	4.5
Salicylic Acid	1.1	1.66

The percentages are calculated upon the concrete.

In the volatile oil Walbaum identified the following compounds:

Eugenol. Characterized by means of its benzoyl compound m. 69°–70°. The phenols present in the oil contained at least 90 per cent of eugenol.

Methyleugenol. Oxidation to veratric acid m. 178°.

Methyl Salicylate. Saponification of the ester gave salicylic acid m. 156°.

Benzaldehyde. Semicarbazone m. 214°.

Anisaldehyde. Semicarbazone m. 203°–204°. Oxidation to anisic acid m. 184°.

Decyl Aldehyde(?). Presence probable.

A Ketone(?). Of violet-like odor.

Benzyl Alcohol. Phenylurethane m. 77°–78°.

Geraniol. Diphenylurethane m. 81°.

Linaloöl(?). Presence probable.

[14] "Les Parfums Naturels," Paris (1939), 201.
[15] *J. prakt. Chem.* [2], **68** (1903), 235. *Ber. Schimmel & Co.*, October (1903), 14.

Digitized by Google Original from CORNELL UNIVERSITY

Use.—When it was still produced in substantial quantities, absolute of *Cassie romaine* served as a lower priced substitute, and occasionally as an adulterant, of absolute of *Cassie ancienne* (see above).

CONCRETE AND ABSOLUTE OF MIMOSA

The name mimosa popularly applies not only to species of the true genus *Mimosa,* of which there are many, but to certain of the genus *Acacia* as well. As a matter of fact, the natural flower oils commercially known as concrete and absolute of mimosa are derived not from any true mimosa, but from *Acacia decurrens* var. *dealbata* (syn. *A. dealbata* Lk.) fam. *Leguminosae.* This tree was introduced to Southern France during the first half of the nineteenth century from Australia, where it is known as "Silver Wattle." Another so-called mimosa is *Acacia floribunda* Willd., cultivated widely in Southern France almost exclusively for the florist trade because of its long-lived flowers. *Acacia decurrens* var. *dealbata,* on the other hand, serves both for the extraction of the oil and for the cut flower trade.

Most mimosas prefer siliceous soils, and do not grow well on calcareous ground. Large forests and groves of mimosa extend along the French Riviera, in the Estérelle and Maures Mountains and in the massif of Taneron (Vallauris, Supercannes, La Croix-des-Gardes, La Bocca, Théoule,

and Mazuyer,[1] the yield of concrete ranges from 0.70 to 0.88 per cent. The perfume is contained exclusively in the flowers. Carefully culled flowers gave as much as 1.06 per cent of concrete against 0.77 per cent from unselected material. The concrete yields from 20 to 25 per cent of absolute.

Physicochemical Properties.—Concrete of mimosa is a solid, waxy mass of light brown color. Its perfume is not strongly characteristic of the live flowers; its odor slightly recalls beeswax. (The concrete derived from *Acacia decurrens* var. *dealbata* exhibits a "by-note" of violet, that from *Acacia floribunda* possesses a phenolic note, reminiscent also of ylang ylang.)

Three concretes described by Naves and Mazuyer[2] (I, II, and III), and by Sabetay and Trabaud[3] (IV) had these properties:

	I	*II*	*III*	*IV*
Melting Point.....	48°	51°	54°	52.5°
Acid Number.....	12.4	16.1	9.8	14
Ester Number.....	32.4	26.2	38.8	38

According to Naves and Mazuyer, the concrete contains from 4.1 to 6.2 per cent of steam-volatile oil. Sabetay and Trabaud reported a yield of 3 per cent of steam-volatile oil. Co-distillation with ethylene glycol *in vacuo* (see Vol. I of this work, p. 215) gives 4.7 per cent of volatile oil.

Absolute of mimosa is a viscous, syrupy liquid of yellow-brownish color, with an odor more typical of the live flowers than is that of the concrete.

Naves and Mazuyer[4] (V), and Sabetay and Trabaud[5] (VI) reported the following values:

	V	*VI*
Specific Gravity at 15°.....	1.002	0.9797
Optical Rotation.....	+22° 40′	+15° 40′
Refractive Index at 20°.....	1.5184	1.5175
Acid Number.....	8.9	28.2
Ester Number.....	60.4	42.3

On co-distillation with ethylene glycol at reduced pressure the absolute

description in these pages. Two volatile oils described by von Soden [6] (I), and Naves, Sabetay and Palfray [7] (II) had these properties:

	I	*II*
Specific Gravity at 15°	0.816	...
Optical Rotation	Inactive or slightly laevorotatory	+0° 35′
Refractive Index at 20°	...	1.4812
Acid Number	12	3.6
Ester Number	20.5	22

Naves, Sabetay and Palfray obtained their oil by vacuum distillation with superheated steam in a specially constructed apparatus.[8]

Sabetay and Trabaud [9] submitted mimosa concrete to steam distillation *in vacuo*, and obtained 3 per cent of a limpid volatile oil with a waxy, fatty, honey-like and "green" odor. The oil exhibited the following properties:

Specific Gravity at 15°/15°	0.8100
Optical Rotation	−0° 30′
Acid Number	14.1
Ester Number	18.2
Ester Number after Formylation	21.2
Methoxy Groups (Zeisel)	1 g. required 0.90 cc. of N/10 $AgNO_3$
Phenols	Traces present
Sulfur and Nitrogen	Absent
Acetylation in Pyridine Solution	Primary and secondary alcohols absent

The typical mimosa odor persisted after the neutralization of the free acids, after oximation. On the other hand, the odor underwent a total change after saponification, the mimosa fragrance giving way to a strong "green" odor of legumes. The really odorous constituents formed only a small fraction both in the product obtained by vacuum distillation and in the concrete. The major portion of the oil consisted of hydrocarbons (see below).

Chemical Composition.—The chemical composition of mimosa flower oil was first investigated by Walbaum and Rosenthal,[10] who identified *anisalde-*

vestigation was carried out by Sabetay and Trabaud [11] (see above) who reported the presence of the following compounds:

Hydrocarbons(?). In crystalline form. Not further identified.

A Hydrocarbon(?). In crystalline form. The properties resembled those of 1-hexadecene $C_{16}H_{32}$.

An Alcohol(?). With a "green" odor, reminiscent of cucumber and ambergris.

Palmitic Aldehyde. Observed for the first time in a natural flower oil. Identified by the oxime m. 86°, and semicarbazone m. 105°–106°.

Enanthic Acid. In the free state. Amide m. 95°.

Anisic Acid. In free state, m. 185°.

Acetic Acid, Palmitic Acid, and Anisic Acid. In ester form.

Phenols(?). Small quantities only, with an odor of leather reminiscent also of pepper.

Use.—Absolute of mimosa is a very interesting and useful natural flower oil that merits much wider application in fine perfumery than it finds at present, particularly in the United States. French perfumers have long recognized its value as an excellent blender and "smoothing agent" for synthetics and as an effective fixative in high-grade perfumes. The odor of absolute of mimosa is mild and smooth; it blends well into scents of floral, as well as of oriental, character. It is one of the lower priced natural flower oils, and therefore can be quite freely employed.

Suggested Additional Literature

R. Arnaud, "Culture des Plantes à Parfums en France," *Ind. parfum.* **4** (1949), 370.

CONCRETE AND ABSOLUTE OF *SPARTIUM JUNCEUM* L.
(Concrete and Absolute of *Genêt*)

There are several species of *Spartium* (fam. *Leguminosae*), popularly known as "Spanish Broom," or "Weavers Broom." In the essential oil industry the most important species is *Spartium junceum* L., known in France as "Genêt d'Espagne." In the south of France it grows wild and

[11] *Perfumery Essential Oil Record* **31** (1940), 123.

Digitized by Google Original from CORNELL UNIVERSITY

abundantly over wide areas, particularly in the Départements Alpes-Maritimes, Var, Basses Alpes, Drôme, and Vaucluse. The plant prefers rocky argillocalcareous soil, and is often found in the company of lavender. The flowers, which appear in June and July, are of beautiful yellow-golden color and exhale a delightful perfume reminiscent of orange blossoms and grape. Bees are greatly attracted to these flowers, with the result that the honey from certain sections of southern France exhibits a decided flavor of *genêt*.

In the Grasse region substantial quantities of the flowers of *Spartium junceum* L. are extracted with petroleum ether. Prior to World War II the quantity of flowers processed reached as much as 50 metric tons yearly; much larger quantities could be processed if demand should warrant it. In the extraction of these flowers it is of fundamental importance to treat them as quickly as possible, because the perfume of the flowers deteriorates rapidly after picking.

In the author's experience, about 1,200 kg. of flowers are required to yield 1 kg. of concrete which, in turn, gives 0.30 to 0.35 kg. of alcohol-soluble absolute. Naves and Mazuyer [1] reported yields of concrete ranging from 0.09 to 1.18 per cent, the concrete giving from 30 to 40 per cent of absolute.

The concrete is a solid, waxy mass of dark brown color, with a most peculiar, "heavy," sweetish and honey-like odor.

For the absolute, a viscous, dark-brown oil of equally peculiar odor, Walbaum and Rosenthal [2] (I), and Sabetay and Igolen [3] (II) reported these properties:

	I	*II*
Acid Number.....	33.6	98.9
Ester Number.....	85.9	81.0

of formic, acetic, and higher aliphatic acids, the alcohols of which exhibit a "green" odor.

Absolute of *genêt* is an interesting flower oil which has to be employed with great skill and discretion to obtain the desired effect. It blends particularly well with absolute of orange flowers (in which it is occasionally used as an adulterant). In the hands of an expert perfumer, absolute of *genêt* imparts remarkable effects to compositions of the heavier type.

CONCRETE AND ABSOLUTE OF *GENISTA TINCTORIA* L.

Genista tinctoria L., syn. *G. sibirica* (fam. *Leguminosae*), the common "Dyers-Greenweed," or "Woodwaxen," grows wild and abundantly in many dry locations, with a mild climate, in Europe and Western Asia. It has been naturalized in North America. Extracting the flowers with low boiling petroleum ether, Treff, Ritter, and Wittrisch,[1] in Germany, obtained 0.161 per cent of a concrete, which yielded 53 per cent of an alcohol-soluble absolute. On steam distillation the concrete gave 2.26 per cent of a yellowish volatile oil with these properties:

Specific Gravity at 15°	0.9335
Optical Rotation	−9° 10′
Acid Number	18
Ester Number	35
Ester Number after Acetylation	156.0

The volatile oil had a "heavy" and "green" odor.

According to the author's knowledge, the concrete and absolute of *Genista tinctoria* are not produced on a commercial scale.

CONCRETE AND ABSOLUTE OF LUPINE

and Wittrisch [1] obtained 0.205 per cent of a concrete which, on treatment with alcohol in the usual way, yielded 60.4 per cent of an alcohol-soluble absolute. The concrete contained 0.95 per cent of a steam-volatile oil with these properties:

Specific Gravity at 15°	0.900
Optical Rotation	+7° 30′
Acid Number	38
Ester Number	31
Ester Number after Acetylation	143

The odor of the volatile oil was penetrating, sweet, and herb-like.

Nothing is known about the chemical composition of the lupine flower oil.

According to the author's knowledge, the oil is not produced on a commercial scale.

[1] *J. prakt. Chem.* [2], **113** (1926), 359.

CONCRETE AND ABSOLUTE OF WISTARIA

Extracting the flowers of *Wistaria sinensis* (Sims) Sweet (fam. *Leguminosae*), called "Glycine" in French, Sabetay [1] obtained 0.197 per cent of a dark brown concrete with these properties: m. 47°, acid number 20, ester number 19.3.

Nothing is known about the chemical composition of this flower oil. The oil is not produced on a commercial scale.

[1] *Ind. parfum.* **5** (1950), 86.

Digitized by Google Original from CORNELL UNIVERSITY

CHAPTER IX

ESSENTIAL OILS OF THE PLANT FAMILY *HAMAMELIDACEAE*

Digitized by Google

Original from
CORNELL UNIVERSITY

Digitized by Google

Original from
CORNELL UNIVERSITY

OIL OF STYRAX

(Oil of Storax)

Essence de Styrax *Aceite Esencial Estoraque* *Storaxöl*
Oleum Styracis

Styrax, or storax, is an aromatic balsam formed and exuded by the styrax tree when the sapwood is injured. The pathological (rather than physiological) exudate congeals upon exposure to air. It is collected for commercial purposes, being widely employed in perfumery, for the scenting of soaps, and in certain medicinal preparations.

There exist on the market two types of styrax, viz., the so-called Levant or Asiatic styrax, and the American styrax, which since World War I has become of much more importance than its Old World prototype. The latter is inferior in quality to the American styrax.

I. Levant or Asiatic Styrax

The oriental sweet gum *Liquidambar orientalis* Mill. (fam. *Hamamelidaceae*) is a native of Asia Minor, in the southwestern parts of which it forms large forests. The tree grows to a height of 20 to 40 ft., in some cases 90 ft.; the smooth leaves are shiny bright green on the upper surface, and pale underneath. The tree grows wild in colonies, the most important of which are located in swampy valleys near the sea, between Makri and Giova. These styrax forests belong to the Turkish government or to private individuals; they are exploited by groups of woodsmen who sell their output to the owners of the forest or to exporters. One foreman and four workers can treat about five hundred trees daily. According to a government

felled for firewood. The shavings collected each day are boiled in water and filtered through coarse cloth bags with the aid of a press. An emulsion of resin and water exudes from the press and is collected. The resin rising to the surface is separated and, while still containing 25 to 30 per cent water, is sold to dealers who remove most of the water and dirt, occasionally also adulterating it with pine resin or oil of turpentine. In normal times the balsam is then sent to Constantinople, Smyrna, and other ports of the Levant, and from these to Marseilles. In 1934, the United States imported more than 35,000 lb. of Levant styrax from Turkey, Italy, and France. Prior to World War I, Anatolia produced from 100,000 to 120,000 kg. of styrax annually (Rollet [2]).

According to Jeancard,[3] young trees yield only a few hundred grams of balsam, older ones from 6.4 to 7.7 kg. At the beginning of the season 10 kg. of shavings are required per kilogram of balsam, in the summer only 5 to 6 kg. During hot spells tears of white styrax can be obtained; their odor is superior to that of ordinary styrax. Quite different from the yields reported by Jeancard are those claimed by Berkel and Hus: [4] 40 to 50 g. of the purified resin from trees forty to fifty years old, 150 to 180 g. from those eighty to ninety years old, 250 to 400 g. from trees one hundred and thirty to one hundred and fifty years old.

Physicochemical Properties of Crude Levant Styrax.—Levant styrax is a semiliquid, sticky, opaque mass of grayish to grayish-brown color which

assaying the content of cinnamic acid has been recommended by van Itallie and Lemkes.[9] The most important principles for the testing of styrax have been described by Anselmino, Seitz and Bodländer.[10] Examining samples of pure styrax from Asia Minor, they found properties varying within these limits:

	Acid Number	*Saponification Number*	*Ester Number*	*Ester Number : Acid Number*
Authentic Crude Styrax..	45 to 61	125 to 147	79 to 92	1.4 to 1.9
Calculated upon Styrax Freed from Water.....	64 to 80	178 to 195	107 to 122	...

These investigators also established the following limits for pure styrax from Asia Minor:

	Per Cent
Loss on Drying	25.5 to 32.5
Water Content	22.3 to 31.5
Alcohol-soluble Portion	64.8 to 72.9
Alcohol-insoluble Portion	1 to 3
Total Cinnamic Acid, Calculated upon Water-free Styrax	21.3 to 25.89
Total Cinnamic Acid	14.6 to 19.4
Free Cinnamic Acid	0.08 to 4.43
Phenol Content	19.93 to 29.42

When examining a sample of styrax according to the methods developed by the above-mentioned authors, the procedures suggested by them must be followed strictly; otherwise divergent results will be obtained. In the United States the most widely used method of analyzing styrax is that official in the United States Pharmacopoeia.

Shipments of crude Levant styrax examined in the laboratories of Fritzsche Brothers, Inc., New York, had properties which varied within these limits:

Loss on Drying	7.0 to 20.0%, in exceptional cases up to 28.0%
Alcohol-soluble Residue	70.0 to 92.5%
Alcohol-insoluble Residue	2.0 to 8.0%
Acid Number of Styrax Purified	51 to 66
Saponification Number of Styrax Purified	168 to 194

The percentage of alcohol-soluble and alcohol-insoluble residue in Levant crude styrax differs considerably from that of American crude styrax. The variation probably results from the age of the Asiatic product, which is usually examined much longer after production than the American styrax. During the long transport from Asia Minor, styrene, an important constituent of the balsam, polymerizes; the resulting polymer is insoluble in alcohol. Therefore, certain allowances should be made in evaluating these factors. In this connection it should also be pointed out that old lots of crude styrax, in which polymerization has taken place to its fullest extent, are most suitable for purification because it is easy to separate the polymerized, alcohol-insoluble portions, and no further polymerization will take place in the purified product.

Incidentally, the technique of sampling styrax is of great importance in evaluating a lot. It is necessary to stir the product thoroughly so that the water will be evenly distributed. If this is not done, the properties obtained will be quite abnormal, and an actually normal product may be rejected.

Physicochemical Properties of Purified Levant Styrax.—For the preparation of *purified* styrax, the crude product is dissolved in 95 per cent alcohol, the insoluble residue is filtered off, and the alcoholic filtrate concentrated. The resulting concentrate, a viscous mass yellow to brown in color, repre-

tained as such, and free, in styrax; the remainder consists of 3 or 4 substances, chiefly a ketone and an easily esterified alcohol.

In 1944, Berkel and Hus [13] reported that the original formula $C_{36}H_{58}O_3$ assigned to "storesin" by von Miller in 1877 is erroneous, the correct formula being either $C_{30}H_{46}O_3$ or $C_{30}H_{48}O_3$. Pure storesin prepared by Berkel and Hus melted at 157°–167°, $[\alpha]_D$ +43° 0′. These two authors arrived at the conclusion that storesin contains a phenolic OH group, but no primary or secondary alcohol group.

The United States Dispensatory [14] still describes storesin, the most abundant constituent of styrax, as an alcohol resin $C_{36}H_{55}(OH)_3$. It is present in two forms, designated respectively α and β, both free and in the form of a cinnamic ester. These together make up from ⅛ to ½ of the resin. Storesin is an amorphous substance m. 168°, readily soluble in petroleum benzin.

Cinnamic Acid. Another important constituent, present in styrax both in free and in ester form. The content of free cinnamic acid ranges from 5 to 15 per cent, but may be as high as 23 per cent.

Cinnamyl Cinnamate ("Styracine"). Styrax contains from 5 to 10 per cent of this ester which can be isolated by repeated extraction with ether, benzene, or alcohol, after the cinnamic acid has been separated from the resin. Cinnamyl cinnamate is volatile only with superheated steam; it crystallizes in tufts of long rectangular prisms m. 44°, which frequently do not form readily. Saponification with concentrated solutions of potassium hydroxide yields potassium cinnamate and cin-

styrax oils. Because of the very low yield from Levant styrax, oil of styrax is now distilled almost exclusively from the American balsam.

Physicochemical Properties.—The volatile oil possesses a light yellow to dark brown color and a pleasant, but peculiar odor. Its properties vary greatly according to the method of distillation employed. The specific gravity of the oil is below 1 if the hydrocarbons predominate, and higher than 1 if the oil contains a high percentage of alcohols and cinnamic esters.

Gildemeister and Hoffmann [15] reported these properties for the oil distilled from Levant styrax:

Specific Gravity	0.89 to 1.06
Optical Rotation	−38° 0′ to +0° 30′
Refractive Index at 20°	1.53950 to 1.56528
Acid Number	0.5 to 33
Ester Number	0.5 to 130
Solubility	Soluble in 1 vol. of 70% alcohol, opalescent on addition of 2 to 5 vol. of 70% alcohol. Soluble in any proportion of 80% alcohol, but the diluted solution often shows opalescence. Oils containing a high percentage of esters are less soluble

Chemical Composition.—The essential oil derived from styrax obviously contains only those constituents of the balsam which are carried over with the steam during distillation. Since some of the components have a high boiling point, the quantitative composition of the oil depends greatly upon the length of distillation, the temperature of the steam, and the steam pressure applied.

The chemistry of the volatile oil from Asiatic styrax was investigated

Phenylpropyl Cinnamate. Identified by von Miller; presence later confirmed by Tschirch and van Itallie.

Cinnamyl Cinnamate ("Styracine"). Also identified by von Miller, and later by Tschirch and van Itallie.

Vanillin. Identified by Dieterich, and later by Tschirch and van Itallie.

It should be mentioned here that oil of styrax contains not only the esters listed above, but also their parent substances, chiefly *phenylpropyl alcohol, cinnamyl alcohol,* and free *cinnamic acid.*

In an oil derived from the bark of the styrax tree, von Soden and Rojahn [22] identified *naphthalene* m. 79°.

II. American Styrax

Liquidambar styraciflua L. (fam. *Hamamelidaceae*), our common sweetgum, or alligator tree, is a beautiful native American tree occurring along the Atlantic Coast from Connecticut southward to Central America. Fully grown, it reaches a height of 100 ft. and sometimes even 150 ft.

There exist two varieties besides the type species. *L. styraciflua* var. *mexicana* has three-lobed leaves, instead of the five- to seven-lobed leaves common to the northern *L. styraciflua* L. *L. styraciflua* var. *macrophylla* of Central America is the second variety; its leaves, also three-lobed, are much larger than those of the type species.

The wood is hard, close-grained, and of a reddish-brown color. The balsam apparently has been long used by the natives; after the conquest by Cortes it was exported to Spain in substantial quantities for use both as a perfume and as a vulnerary. The balsam, commonly known as liquidamber

50 in. in exceptional cases. It grows wild in the enormous forests of Honduras and nearby parts of Guatemala. The trees usually occur in large stands at elevated altitudes between the tropical jungles in the valleys and the pine forests of the high mountains. A *Liquidambar* tree can readily be recognized in the fall by the color of its leaves, which turn red.

The styrax is a pathological exudate and not all trees contain it. As many as 15 trees may be examined in vain before one containing balsam is found. Small pockets develop beneath the bark, and gradually increase in size; in these the balsam accumulates. The collectors of the balsam go from tree to tree, examining each for pockets. To ascertain whether balsam is actually present in a pocket they hit the bark with a wooden mallet, the sound then indicating whether the pocket should be tapped. If the pocket is located high and not easily accessible the woodsmen are tempted to fell the tree to get at the pocket. In fact, this was the method practiced formerly. Of late, however, felling of the trees has been prohibited by the government because a felled *Liquidambar* tree represents an economic loss, as the wood cannot be hauled out of the forests. Moreover, when a *Liquidambar* tree is cut down it usually breaks at its weakest point, i.e., at the location of the pocket, and as the tree crashes down the pocket breaks open

skins. After the styrax has reached the first outposts of civilization it must be transported to Tegucigalpa, capital of Honduras. Since no road exists between Olancho and Tegucigalpa this has to be accomplished by air freight; in fact, even the empty drums have to be shipped by air from Tegucigalpa to Olancho—and the freight charge is calculated by volume, not by weight of the empty drums. From Tegucigalpa the exporters then send the drums of styrax by rail or road to an Atlantic or Pacific seaport, for transshipment to the United States or Europe.

As was mentioned above, most of the Honduran styrax originates from the Olancho region. According to information gathered by the author in 1950 while surveying production of styrax in Honduras, collection of styrax in the various regions of Honduras is distributed as follows:

	Per Cent
Olancho	99.0
Comayagua	0.7
Progresso	0.2
Santa Barbara	0.1
	100.0

Total yearly production of styrax in Honduras averages about 100 drums (one drum = 520 lb.).

B. Guatemala Styrax.—During World War II small quantities of styrax were collected in areas adjoining Honduras. After the war, however, production diminished almost to the vanishing point; the following account is, therefore, given merely for completeness' sake.

According to Schaeuffler,[24] the producing regions of styrax (*Estoraque* or *Liquidambar*) in Guatemala are located in the Departments of Alta Verapaz, Zacapa, and Chiquimula. The tree from which the balsam is

sapwood in a "V" shape. These strips induce the flow of balsam, which runs along the strips into the groove from where it is removed with a spoon and transferred into a tin or any other receptacle. At first it takes two to three months, depending on weather conditions, for the groove to fill up, but later the balsam flows more freely. After approximately nine months, additional strips are peeled off and the old ones scrapped, which procedure opens up new passages for the flow of balsam. On old trees as many as six to ten grooves with their corresponding strips can be cut at different heights.

(*b*) *Deposit Method.*—Many *Liquidambar* trees have natural deposits of balsam beneath the bark, probably provoked by some injury to the sapwood by insects. These deposits can be detected by outgrowths on the tree trunk and also by the texture of the veins; in either case quite some experience is required to locate trees which have natural deposits. If these deposits are at a height which can be reached from the ground, a hole is drilled and the balsam which flows from the deposit is collected in a container. If the deposit cannot be reached from the ground, the tree must be felled and tapped on the ground.

The collected balsam is heated in a water bath, whereby coarse impurities, such as particles of bark, sapwood, and bugs, rise to the surface and are removed. While still hot, the balsam is roughly filtered through cheesecloth to remove the finer impurities, and then stored in five-gallon tins or

Physicochemical Properties of American Styrax

In the crude state, American styrax is a gray, occasionally pale brown, viscous mass, usually free flowing, but sometimes a semisolid substance, which softens on gentle warming. It often shows separation of water and contains specks of impurities or foreign matter. The crude balsam contains much less water than the corresponding Asiatic product and is, therefore, of higher quality. Crude American styrax imported from Honduras and Guatemala and analyzed by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Loss on Drying	7.0 to 27.0% (seldom over 15%)
Alcohol-soluble Residue	70.8 to 95.0% (seldom less than 85%)
Alcohol-insoluble Residue	0.2 to 6.8% (seldom over 5%)
Acid Number of Styrax Purified	36 to 52.3
Saponification Number of Styrax Purified	160 to 194

The alcohol-insoluble portions of certain lots of American styrax occasionally exceed 5 per cent. This is an indication of the age of the material and is caused by polymerization of styrene.

Commercially purified American styrax prepared by Fritzsche Brothers, Inc., New York, exhibited the following properties:

Acid Number	35.5 to 47.6
Saponification Number	164 to 186

Purified American styrax is usually a clear, viscous liquid of brown color

As regards congealing point, these oils did not readily congeal and temperatures ranging from −10° to −20° or even lower were required to bring about congelation.

Chemical Composition.—The chemical composition of American styrax and its volatile constituents was investigated by von Miller,[27] Tschirch and van Itallie,[28] Thoms and Biltz,[29] Hellström,[30] Burchhardt,[31] and Tschirch and Werdmüller.[32] The presence of the substances reported by these workers was later confirmed by Schimmel & Co.[33] in the *volatile oil* derived from American styrax:

Hydrocarbons(?). Among them compounds of the empirical molecular formula C_8H_8, C_8H_{10} and C_9H_{12}.

Styrene. Identified by von Miller through its dibromide m. 73° (cf. Chemical Composition of "Asiatic Styrax Oil").

Cinnamic Acid. Free and in esterified form (Schimmel & Co.).

Cinnamyl Alcohol. Free and in esterified form (Schimmel & Co.).

Phenylpropyl Alcohol. Also free and in esterified form (Schimmel & Co.).

Phenylpropyl Cinnamate. First reported by von Miller; presence later confirmed by Schimmel & Co.

Cinnamyl Cinnamate ("Styracine"). Also first reported by von Miller, and later by Schimmel & Co.

A Sesquiterpene(?). B. 261°–262° (Schimmel & Co.).

Vanillin. Presence in small quantities probable.

Use

Styrax is seldom employed today in medicinal preparations, except as a constituent of the compound tincture of benzoin.

Styrax is a valuable raw material for the isolation of cinnamyl alcohol

OIL OF *HAMAMELIS VIRGINIANA* L.
(Oil of Witch Hazel)

On simple steam distillation the leaves and terminal branches of *Hamamelis virginiana* L. (fam. *Hamamelidaceae*) yield not an essential oil but an aromatic water, viz., the popular witch hazel, used widely as an after-shaving lotion and in certain toilet preparations.

Little is known about the odoriferous principles of this distillate. To isolate the (concentrated) volatile oil of *Hamamelis virginiana* L., it would probably be necessary to cohobate the distillation waters (witch hazel) repeatedly, until the oil separates clearly from the water. Very probably most of the odoriferous constituents of the oil are soluble in large quantities of water, as is the case with oil of rose, which can be recovered fully only by repeated cohobation of the distillation waters.

Scoville,[1] and Jowett and Pyman[2] investigated small quantities of oil and observed the presence of an alcohol (about 7 per cent), of an ester $C_{10}H_{17}\cdot COOCH_3$ (7.3 per cent), low molecular fatty acids (0.6 per cent), high molecular fatty acids (small quantities), phenols with an odor of eugenol, a sesquiterpene $C_{15}H_{24}$, b. 259°–260°, α_D +14° 53′, solid waxes and paraffins, and a compound with an odor of safrole.

Suggested Additional Literature

S. L. Hilton, "*Aqua Hamamelidis* N. F. Witch Hazel Water," *J. Am. Pharm.*

Digitized by Google
Original from
CORNELL UNIVERSITY

Digitized by Google

Original from
CORNELL UNIVERSITY

OIL OF GURJUN BALSAM

Gurjun balsam is the pathological exudation, caused by incision or scorching with fire, of the wood of several species of *Dipterocarpus* (fam. *Dipterocarpaceae*). There are about fifty species of this genus, tall and beautiful trees which grow wild in the mountain forests of India, Burma, and Indo-China. A fully grown tree yields as much as 180 liters of balsam during a summer. The balsam is obtained like gum turpentine. Large quantities are used in Indian varnishes. The trade often refers to gurjun balsam as "East Indian Copaiba Balsam," but this is a misnomer. Other vernacular terms are "Wood Oil" (in India[1]) and "Huile de Bois" (in French Indo-China).

In India and Burma there are two types of gurjun balsam, viz., the "Kanyin Oil," derived chiefly from *Dipterocarpus turbinatus* Gaertn., and the "In Oil," obtained principally from *D. tuberculatus* Roxb.[2] The former is the true gurjun balsam; "Kanyin Oils" are obtained by hacking triangular holes into the base of the live trees, scorching the opening with

On steam distillation gurjun balsam yields from 60 to 75 per cent of volatile oil.

Physicochemical Properties of Gurjun Balsam Oil. The volatile oil

oil (I) of balsamic odor. The second balsam originated from *D. turbercu-latus* Roxb., and on steam distillation gave 33 per cent of a yellowish-brown oil (II). The two oils exhibited these properties:

	I	*II*
Specific Gravity at 15°	0.9271	0.9001
Optical Rotation	−37° 0′	−99° 40′
Refractive Index at 20°	1.50070	1.50070
Acid Number	0	0
Ester Number	1.9	0
Solubility in 95% Alcohol	Soluble in 7 and more vol.	Soluble in 6 and more vol.

Chemical Composition of Gurjun Balsam Oil.—Oil of gurjun balsam consists chiefly of sesquiterpenes of closely similar boiling points. Fractionating an oil at atmospheric pressure (741 mm.), Schimmel & Co.[9] obtained 86 per cent of a fraction boiling between 260° and 265°, and 6 per cent of a fraction boiling from 265° to 269°.

The principal constituents of gurjun balsam oil are α- and β-*gurjunene* (cf. Vol. II of the present work, p. 119); in fact rectified gurjun balsam oil represents little more than a mixture of α- and β-gurjunene (Gildemeister and Hoffmann).

Pfau and Plattner[10] have reported that gurjun balsam oil contains a mixture of *sesquiterpenes* and *sesquiterpene alcohols* (b_{10} 127°–128°, d_{20} 0.9140, α_D −179° 30′, n_D^{20} 1.5010); on dehydrogenation with sulfur or selenium, this mixture yields S-guaiazulene.

Use.—At one time, gurjun balsam oil was used quite extensively as a fixative of perfume compounds in the scenting of soaps and technical products. Occasionally the oil was also employed as an adulterant of

of Chinese, who ship the borneocamphor to Singapore, Penang, Hong Kong, and India. Despite its much higher price, the Chinese and Malayans still prefer the natural borneol to the synthetic product for use in rituals.

As was mentioned above, borneocamphor trees also contain an essential oil, the so-called borneocamphor oil. An oil from Singapore examined by Schimmel & Co.[5] had these properties:

Specific Gravity at 15°	0.9180
Optical Rotation	+11° 5′
Refractive Index at 20°	1.48847
Acid Number	5.6
Ester Number	0
Ester Number after Acetylation	50.5, corresponding to 17.67% of ester $C_{10}H_{17}OCO \cdot CH_3$
Solubility	Soluble in 5 vol. and more of 90% alcohol, with slight turbidity

The oil had a dark brown color and an odor reminiscent of turpentine and borneol. Investigating the chemical composition of this oil, Schimmel & Co. found its composition to be approximately as follows:

Digitized by Google
Original from
CORNELL UNIVERSITY

CHAPTER XI

ESSENTIAL OILS OF THE PLANT FAMILY *ANONACEAE*

Digitized by Google

Original from
CORNELL UNIVERSITY

Digitized by Google
Original from
CORNELL UNIVERSITY

OIL OF CANANGA

Essence de Cananga *Aceite Esencial Cananga* *Canangaöl*
Oleum Canangae

Botany and Occurrence.—*Cananga odorata* Hook. f. et Thomson, syn.

tained from the same botanical source as cananga oil, and whether the

the earthen pot becomes too warm, cold water is added. The oil separator

per cent) price than the Bantam oil. As a matter of fact, the perfume of

The root oil is a yellowish-green, crystalline mass of buttery consistency, and has a disagreeable, bitter, at first burning, and then cooling, flavor. The odor of the herb oil is not strongly characteristic.

Little is known about the physicochemical properties of the oils derived from the roots and the overground parts of the plant, probably because these oils have no commercial importance.

As regards the chemical composition, Schimmel & Co.[2] years ago noted the presence of *cineole* in the *herb* oil.

More recently Stavholt and Sörensen[3] steam distilled 5.5 kg. of *roots* of *Artemisia vulgaris*, obtaining 1.1 g. of essential oil, in which they noted the presence of *dehydromatricaria ester* (methyl *n*-decenetriynoate), $C_{11}H_8O_2$, m. 113°. This ester is assumed to possess either of the following structural formulas:

$$CH_3 \cdot CH{=}CH \cdot C{\equiv}C \cdot C{\equiv}C \cdot C{\equiv}C \cdot COOCH_3$$

or

$$CH_3 \cdot C{\equiv}C \cdot C{\equiv}C \cdot C{\equiv}C \cdot CH{=}CH \cdot COOCH_3$$

So far as the author knows, the oil has never been produced commercially.

[2] *Ibid.*
[3] *Acta Chem. Scand.* **4** (1950), 1567. *Chem. Abstracts* **45** (1951), 7005.

OIL OF *BLUMEA BALSAMIFERA* DC.

Blumea balsamifera DC., a shrub-like plant of the family *Compositae*, is a native of India; it occurs wild from the Himalaya Mountains to Singapore, in Burma, Tonkin, South China, Formosa, Hainan, in the Malayan Archipelago, and the Philippine Islands.

The stalks and leaves of the plant contain from 0.1 to 0.4 per cent of an essential oil which can be isolated by hydrodistillation.[1,2] Experiments carried out by the Indian Forest Department yielded as much as 1.88 per cent of oil.[3]

According to Gildemeister and Hoffmann,[4] the so-called "Ngai-camphor"

[1] Bacon, *Philippine J. Sci.* **4A** (1909), 127.
[2] Cayla, *J. Agr. Tropicale* **8** (1908), 30; **9** (1909), 251. *Ber. Schimmel & Co.*, April (1908), 154. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 956.
[3] *Perfumery Essential Oil Record* **3** (1912), 341.
[4] "Die Ätherischen Öle," 3d Ed., Vol. III, 956.

Digitized by Google Original from CORNELL UNIVERSITY

obtained by distillation of the plant in the Province of Kwangtung (China) and on the Island of Hainan (China) is used locally for ritual and medicinal purposes. As much as 15,000 lb. per year are said to have been exported at one time from Hainan, whereas in the south of China (Kwangtung) up to 18,000 lb. were produced. The crude product was refined in Canton.[5,6]

In 1895, Schimmel & Co.[7] examined a sample of Ngai-camphor and found that the yellow-white, crumbly, crystalline mass consisted almost entirely of pure *l*-borneol. That Ngai-camphor is actually identical with laevorotatory borneol had already been reported years ago by Plowman,[8] and by Flückiger.[9]

In 1909, Jonas [10] examined a dark brown Ngai-camphor oil of characteristic borneol-like odor; most of the borneol, however, had probably been already removed from the oil by steam distillation. In this oil (d_{15} 0.950, α_D −12° 30′, n_D^{20} 1.48151, acid number 23.35, ester number 1, ester number after acetylation 198, total alcohol content, calculated as $C_{10}H_{18}O$, 63.95 per cent) Jonas [11] established the presence of the following compounds:

Cineole.

Limonene.

l-Borneol.

l-Camphor.

Phloracetophenone Dimethyl Ether.

Sesquiterpenes (b. ~280°).

Sesquiterpene Alcohols (b. ~280°).

Palmitic Acid (presence probable).

Myristic Acid (presence probable).

For details regarding the phloracetophenone dimethyl ether, see Vol. II of the present work, p. 543.

In 1910, Schimmel & Co.[12] investigated a Ngai-camphor which had been distilled in Dehra Dun (India) from air-dried leaves and found that it contained 75 per cent of *l*-camphor, 25 per cent of *l*-borneol, and minute quantities of a yellowish oil. Schimmel & Co. could not explain why some lots of Ngai-camphor consisted exclusively of *l*-borneol, and other lots of

[5] Holmes, *Pharm. J.* [3], **21** (1891), 1150.
[6] Cayla, *J. Agr. Tropicale* **13** (1913), 317. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 956.
[7] *Ber. Schimmel & Co.*, April (1895), 74.
[8] *Pharm. J.* [3], **4** (1874), 710.
[9] *Ibid.*, 829.
[10] *Ber. Schimmel & Co.*, April (1909), 149.
[11] *Ibid.*
[12] *Ibid.*, April (1910), 149.

Digitized by Google
Original from CORNELL UNIVERSITY

a mixture of *l*-borneol and *l*-camphor. The reason may be that the product was sometimes distilled exclusively from *Blumea balsamifera* DC., and sometimes from a mixture with other *Blumea* species—*lacera* DC., for example.

In 1925, Chiris [13] analyzed a distillate of *Blumea balsamifera* DC., obtained near Langson (Tonkin), where the plant is called "Dai-bi." The distillate contained chiefly *d*-camphor and only 1.54 per cent of borneol. In the opinion of Gildemeister and Hoffmann [14] the presence of *dextrorotatory* camphor in Ngai-camphor is most unusual and may be explained probably by ample addition of ordinary *d*-camphor to the product in question.

OIL OF CHAMOMILE

(Roman or English Chamomile Oil)

Essence de Camomille Romaine *Aceite Esencial Manzanilla Romana*
Römisch-Kamillenöl *Oleum Chamomillae Romanae*
Oleum Anthemidis

Anthemis nobilis L. (fam. *Compositae*), the so-called Roman or English chamomile, is an herbaceous composite with a perennial root. The stems are from 6 to 12 in. long, trailing, and divided into branches which turn upward at their extremities. The flowers are solitary, possessing a yellow, convex disc and white rays. The plant, native to Europe, is cultivated in Belgium, France, and England. Belgium is the principal producer of chamomile, with areas of cultivation located chiefly near Lessines and Flobecq in the province of Hainaut, and near Grammont in the province of East Flanders. In the United States chamomile occurs wild in certain regions, or serves as an ornamental plant in gardens, especially along borders. It blossoms from mid-summer until killed by frost.

Roman chamomile grows well in almost any good, fairly dry soil, with full exposure to the sun. It prefers temperate climates and must be protected from the rigors of adverse weather.

Dafert and Brandl [1] showed that *Anthemis nobilis* gives a maximum yield of flowers and oil when supplied with artificial fertilizers (125 g. Chile

[13] *Parfums France* (1925), 257.
[14] "Die Ätherischen Öle," 3d Ed., Vol. III, 959.
[1] *Angew. Botan.* **12** (1930), 212.

Digitized by Google Original from CORNELL UNIVERSITY

saltpeter, 395 g. superphosphate, and 100 g. potassium salt per 10 sq. m.), or with ample organic fertilizers. The Roman chamomile behaves similarly to the German chamomile (*Matricaria chamomilla* L.): great sensitivity to unbalanced phosphatic fertilizers and preference for potassium. Yield of oil appears to depend on the growth of the plant as a whole.

Anthemis nobilis is a difficult crop, and requires careful handling. In Belgium, much of the work of cultivation and harvesting is done by women and children as a sort of family industry. The plant is set out in the fields in the first warm days of spring. Propagation may be by seed or by root cuttings. Root divisions are planted in straight lines, with spacing of about 50 cm. between the plants, and 60 cm. between the rows. As the herb grows, it develops numerous clustered, curved stalks about 40 cm. high, which almost completely cover the ground, so that weeding is rarely necessary. The ends branch out and bear the flowers, which are gathered during dry, clear weather as they mature. The young flower buds continue to develop into full-grown flowers, to be gathered later in the season.

The flowers are harvested about every two weeks, by women and young girls, who kneel between the rows and with both hands skillfully pick them. The larger ones are first collected in wicker baskets and from there emptied into sacks standing along the fields. A season's harvest consists of about five or six pickings in each field. The flowers of the second and third pickings are usually the most beautiful and contain the most essential oil. In view of the great number of small fields, there are fresh flowers available almost every day of good weather. In Belgium the harvest lasts about two and a half months, from the end of July to the middle of October.

Harvesters are paid according to weight of fresh flowers gathered. Growers sell the fresh flowers to herb exporters, whose trucks daily collect the sacks of chamomile flowers harvested during the day. The material is transported as quickly as possible to the kilns, where large quantities of flowers can be dried with hot air within a few hours.

Five kilograms of fresh chamomile flowers yield about 1 kg. of dried flowers, but the ratio varies considerably with the season. In dry, sunny weather, the flowers are very beautiful, large and pure white, whereas during rainy, damp weather they appear grayish or rusty.

The cultivation of Roman chamomile is a relatively important industry in Belgium. It extends over a territory comprising more than twenty communities, and is carried out by several hundred families, all of whose members participate, since a good deal of work is involved.

Before World War II, Belgium produced from 200 to 250 metric tons of dried flowers annually. These were exported for distillation in other countries (chiefly France). Within the last few years, the Belgians have made attempts to carry out distillation locally; the new essential oil industry

Digitized by Google
Original from CORNELL UNIVERSITY

does not appear, as yet, to have reached major proportions. However, with time and experience Belgium ought to be able to produce several oils, of excellent quality, particularly from domestically grown aromatic plants such as chamomile, angelica, valerian and hops.

It appears doubtful whether *Anthemis nobilis* could be successfully cultivated on a large scale in the United States, as the crop requires much hand labor. Under normal conditions, such labor is expensive in the United States, and competition with the low-priced European labor does not seem feasible.

According to Gildemeister and Hoffmann,[2] steam distillation of the whole plant yields from 0.2 to 0.35 per cent of oil. Flowering heads alone give a higher yield (up to 1 per cent). Dried flowers distilled in France, under the author's supervision, yielded from 0.32 to 1 per cent of oil.

Physicochemical Properties.—Freshly distilled Roman chamomile oil has a light blue color which, on prolonged standing and exposure to air and light, gradually changes first to green and later to yellow-brown. The odor of the oil is strong, aromatic, and characteristic of the flowers; the flavor is slightly burning.

Gildemeister and Hoffmann [3] reported these properties for Roman chamomile oil:

Specific Gravity at 15°	0.905 to 0.918
Optical Rotation	−1° 0′ to +3° 0′; in most cases too dark for determination [4]
Refractive Index at 20°	1.442 to 1.457
Acid Number	1.5 to 14
Ester Number	210 to 317
Solubility	Soluble in 5 to 10 vol. of 70% alcohol, occasionally with turbidity. Soluble in 1 to 2 vol. of 80% alcohol, occasionally with turbidity and separation of paraffins

Oils distilled under the author's supervision in Seillans (Var), France, from Belgian and French flower material, exhibited properties varying within the following limits:

Specific Gravity at 15°	0.904 to 0.912
Optical Rotation	−0° 40′ to +0° 48′
Refractive Index at 20°	1.4410 to 1.4461
Acid Number	4.2 to 11.2

[2] "Die Ätherischen Öle," 3d Ed., Vol. III, 976.
[3] *Ibid.*
[4] The use of sodium vapor lamps is recommended (see Vol. I of the present work, p. 242).

Digitized by Google Original from CORNELL UNIVERSITY

sufficiently for the deposit to reliquefy and flow off. Great care must be exercised in doing this.

Certain constituents of the oil are soluble in large quantities of warm water; moreover the oil has a high specific gravity and tends to flow off with the distillation water in the form of a milky emulsion. For these reasons the distillation waters must be redistilled (cohobated); by this means as much as 30 per cent of the total oil distilled over may be recovered.

Yield of Oil.—Foreign, particularly German, chemical literature contains numerous references to investigations of the various methods of assaying the volatile oil content of chamomile flowers, and of the yield of oil obtained from different qualities of flower material. To cite only the more recent works:

Kaiser, Eggensperger and Bärmann [2] found that whole German flowers contained from 0.6 to 0.67 per cent of a deep blue oil; whole Hungarian flowers from 0.3 to 0.35 per cent.

Bergmann [3] reported 0.72 to 0.78 per cent of oil from German flowers, and 0.38 to 0.63 per cent from Hungarian material.

Rom [4] obtained these yields of oil from Hungarian flowers:

(a) 0.35 to 0.38 per cent from poorly dried material,
(b) 0.41 to 0.84 per cent from medium to high-grade material.

Gstirner [5] suggested an improvement in the official German assay (Deutsches Arzneibuch VI). He found that pulverized flowers yield more oil than whole flowers.

Liebisch [6] observed these yields of oil from:

	Per Cent
Yugoslavian flowers	0.39–0.56
Hungarian flowers	0.43–0.54
German flowers	0.70–1.05

Improvements in the official German assay were suggested also by Kleinert and Zimmermann [7] (who reported yields of 0.75 to 1.05 per cent from 12 samples of flowers), and by Peyer.[8]

Will [9] reported 0.5 to 1.5 per cent of oil from German flowers, and widely varying yields from Hungarian material. Most of the Yugoslavian flowers gave a poor yield. Two Greek samples gave 0.56 and 0.44 per cent of oil

[2] *Süddeut. Apoth. Ztg.* **68** (1928), 284. *Chem. Zentr.* (1928), II, 1234.
[3] *Pharm. Zentr.* **71** (1930), 785.
[4] *Pharm. Post* **66** (1933), 109.
[5] *Apoth. Ztg.* **48** (1933), No. 70.
[6] *Chemistry Industry* **57** (1934), 762.
[7] *Pharm. Ztg.* **81** (1936), 1091.
[8] *Deut. Apoth. Ztg.* **52** (1937), 247.
[9] *Ibid.* **53** (1938), 1479.

Digitized by Google
Original from CORNELL UNIVERSITY

with an abnormal odor. Spanish flowers yielded 0.31 per cent of a colorless oil with a fruity odor.

Determining the volatile oil content of 84 chamomile samples originating from 10 different regions, Heeger and Rosenthal [10] obtained yields ranging from 0.25 to 1.35 per cent, the average being 0.48 per cent.

As regards the yield of oil from large-scale industrial distillation, Gildemeister and Hoffmann [11] claim that the most suitable flower material comes from Hungary, and that the yield of oil ranges from 0.2 to 0.38 per cent. According to de Bittera,[12] Hungarian producers obtain from 0.2 to 0.5 per cent, on the average 0.3 per cent, of oil. Distilling dried Hungarian chamomile flowers in Seillans (Var), France, the author of the present work observed yields varying between 0.1 and 0.4 per cent. German chamomile flowers distilled by Schimmel & Co.[13] yielded 0.25 to 0.425 per cent of oil.

Physicochemical Properties.—The oil derived from *Matricaria chamomilla* L. is a deep blue liquid of strong and characteristic odor, and bitter aromatic flavor. Depending upon the temperature, it is more or less viscous. Under the influence of light and air the deep blue color of the oil gradually changes to green, and finally to brown.

Gildemeister and Hoffmann [14] reported these properties:

Specific Gravity at 15°	0.917 to 0.957 (0.9586 in the case of one oil distilled from whole flowers)
Acid Number	5 to 50
Ester Number	3 to 39
Ester Number after Acetylation	117 to 155
Solubility	Even in 95% alcohol soluble only with more or less pronounced separation of paraffins

Some oils are quite viscous even at 15° and at that temperature commence separating crystals; the specific gravity of such oils has to be determined in their superfused state. According to Gildemeister and Hoffmann,[15] oils of chamomile, despite literature reports to the contrary, do not assume a buttery consistency on cooling, and do not congeal, at 0°, to a solid mass. Oils distilled by Schimmel & Co. were only viscous even at −20°; none solidified, none had even a butter-like consistency at this temperature. However, a sample of pure German chamomile oil, examined by Fritzsche Brothers, Inc., congealed to a solid mass when cooled to 0° C.

[10] *Pharmazie* **4** (1949), 385.
[11] "Die Ätherischen Öle," 3d Ed., Vol. III, 985.
[12] Private information of Dr. Jules de Bittera, Budapest.
[13] *Ber. Schimmel & Co.* (1939), 39.
[14] "Die Ätherischen Öle," 3d Ed., Vol. III, 987.
[15] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

(*Top*) German chamomile (*Matricaria chamomilla*) growing wild in Farmos, Com. Pest, Hungary. (*Middle*) A plantation of Roman chamomile (*Anthemis nobilis*) near Deáki (Pozsony County), Hungary. *Photos Dr. Jules de Bittera, Budapest, Hungary.* (*Bottom*) Harvest of Roman chamomile (*Anthemis nobilis*) in Belgium. *Photo Fritzsche Brothers, Inc., New York.*

Digitized by Google
Original from CORNELL UNIVERSITY

and lime-containing soils in southern France. The oil obtained by Chiris had these properties:

Specific Gravity at 15°	0.9546
Optical Rotation	−6° 26′
Refractive Index at 20°	1.4908
Acid Number	9.12
Ester Number	22.41
Ester Number after Acetylation	126.25
Solubility	Soluble in 0.1 vol. of 95% alcohol

Years ago, Chiris had examined also a dextrorotatory santolina oil (α_D +10° 50′).

Chemical Composition.—The volatile oil derived from *Santolina chamaecyparissus* L. contains a terpene(?), b. 165°–170°, in the first fractions, and perhaps a phenolic ether. The chief constituent is a mixture of two unsaturated ketones $C_{10}H_{16}O$, viz., *α-* and *β-santolinenone,* which have been investigated by Francesconi and his collaborators. (For details see Vol. II of the present work, p. 409.) The third isomer appears to be a saturated ketone $C_{10}H_{16}O$, which is probably of the camphor type.

Use.—According to the author's knowledge, the essential oil of *Santolina chamaecyparissus* L. is not produced on a commercial scale.

OIL OF TAGETES

The common term "marigold" embraces a diversity of plants with golden flowers, most of which belong to the family *Compositae.* Prominent among the marigolds are various species of *Tagetes,*[1] particularly *Tagetes glandulifera* Schrank, an annual herb, which, according to the "Handlist of Herbaceous Plants," [2] is synonymous with *Tagetes minuta* L.[3]

[1] For a detailed discussion, see *Parfums France* **14** (1936), 6.

[2] Royal Botanic Gardens, Kew (1925).

[3] In 1924 the Imperial Institute, London [*Bull. Imp. Inst.* **22** (1924), 279] examined an essential oil distilled in Africa, supposedly from *Tagetes minuta* L., and found these properties: d_{15} 0.9369, α_D +1° 42′, n_D^{20} 1.496, Acid Number 1.5, Ester Number 44.5, Ester Number after Acetylation 116.5; soluble in 1.5 volumes of 90% alcohol, turbid on dilution. The oil polymerized rapidly on standing. The Imperial Institute also reported the presence, in this oil, of olefinic terpenes (myrcene or ocimene?), small amounts of phenols, linaloöl, and carvone, without, however, indicating how

Digitized by Google Original from CORNELL UNIVERSITY

Specific Gravity at 15°/15°	0.917 to 0.951
Optical Rotation	Too dark to be determined, even in a short tube
Refractive Index at 20°	1.4600 to 1.4829
Saponification Number	30.0 to 203.4
Ester Number after Acetylation	56.4 to 237.0
Ketone Content, Calculated as Thujone (Hydroxylamine Hydrochloride Method)	6.9 to 69.2%
Solubility	Soluble in 1 to 1.5 vol. of 80% alcohol, clear to turbid with more. Some oils insoluble in 10 vol. of 80% alcohol

These limits, obviously quite wide, are those of pure oils distilled at various stages of plant development. The properties of the best North American oils, in the author's experience, lie within the following, more narrow limits:

Specific Gravity at 15°/15°	0.921 to 0.937
Optical Rotation	Too dark to be determined, even in a short tube
Refractive Index at 20°	1.4600 to 1.4730
Saponification Number	30.8 to 110.1
Ester Number after Acetylation	77.0 to 141.4
Ketone Content, Calculated as Thujone (Hydroxylamine Hydrochloride Method)	40 to 69%
Solubility	Soluble in 1 to 1.5 vol. of 80% alcohol, clear to turbid with more. Some oils insoluble in 10 vol. of 80% alcohol

Because of the dark color of the oil, the optical rotation cannot be determined, even in a very short polariscopic tube. However, using 1 per cent alcoholic solutions of all sorts of commercial wormwood oils, Gildemeister and Hoffmann [3] found dextrorotations ranging from +40° to +70° (calculated for the undiluted oils). An oil distilled in Barrême (B.A.), France, from *wild* growing herb exhibited a laevorotation of −16° 40′ (determined in a 1 per cent alcoholic solution, and calculated for the undiluted oil).

The ketone content of the oil (calculated as thujone) is assayed by the hydroxylamine hydrochloride method. For details see Vol. I of the present work, p. 285.

As regards wormwood oils produced abroad, Gildemeister and Hoffmann [4] reported these properties for commercial oils from France, Algeria and Italy:

[3] "Die Ätherischen Öle," 3d Ed., Vol. III, 1012.
[4] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

	French Oils	*Algerian Oils*	*Italian Oils*
Specific Gravity at 15°.....	0.901 to 0.954 (usually above 0.92)	0.905 to 0.939	0.918 to 0.943
Refractive Index at 20°.....	1.46684 (1 determination)	...	...
Acid Number.....	Up to 6.7	Up to 6.1	Up to 5.6
Ester Number.....	11 to 108 (in one case 135)	14 to 93	15 to 37
Ester Number after Acetylation.....	...	...	123.2
Solubility in 80% Alcohol...	Soluble in 1 to 2 vol., occasionally turbid with more alcohol. Some oils insoluble		
Solubility in 90% Alcohol...	Clearly soluble, either from the beginning or in 0.5 to 1 vol. In rare cases turbid on dilution		

The same authors also described the properties of wormwood oils distilled by Schimmel & Co. in Miltitz, Germany, from Hungarian herb material (I and II), native Miltitz material (III), and French plants grown in Miltitz (IV):

	I	*II*	*III*	*IV*
Specific Gravity at 15°.....	0.8845	0.9125	0.932 to 0.954	0.9276 to 0.9331
Acid Number.....	...	16.8	0.2 to 8.6	Up to 1.5
Ester Number.....	35.0	75.4	76 to 185	38.8 to 65.3
Ester Number after Acetylation.....	...	...	153 to 222	93.3 to 170.3
Solubility.....	Insoluble in 80% alcohol. Easily soluble in 90% alcohol	Insoluble in 80% alcohol. Soluble in 90% and in 95% alcohol; first clearly, but with turbidity on dilution	Usually soluble in 1 to 4 vol. of 80% alcohol. Soluble in all volumes of 90% alcohol; in a few cases 0.5 to 1 vol. required for clear solution	Soluble in 1 to 1.5 vol. of 80% alcohol, in one case turbid on dilution. Soluble in all volumes of 90% alcohol

The bulk of oil (III) distilled from 36° to 90° at 4 mm.; all fractions exhibited strong dextrorotation (+55° to +75°).

Gildemeister and Hoffmann [5] also reported on the properties of oils distilled in Barrême (B.A.), France, from wild growing plants, and from cultivated plants:

[5] *Ibid.*

Digitized by Google Original from CORNELL UNIVERSITY

Stilbene, 218
Storax, *see* Styrax
"Storesin," 246
"Styracine" (cinnamyl cinnamate), 247, 249, 254
Styrax, American, *249*
Styrax, American—chemical composition, *246*, *254*
Styrax, American—physicochemical properties, *253*
Styrax, American—use, *254*
Styrax, Asiatic, *see* Styrax, Levant
Styrax, Guatemala, *249*
Styrax, Honduras, *251*
Styrax, Levant, *243*
Styrax, Levant—chemical composition, *246*
Styrax, Levant—physicochemical properties (crude), *244*
Styrax, Levant—physicochemical properties (purified), *246*
Styrax, Levant—use, *254*
Styrax oil, *243*
Styrax oil, American, *253*
Styrax oil, American—use, *254*
Styrax oil, Asiatic, *see* Styrax oil, Levant
Styrax oil, Levant, *247*
Styrax oil, Levant—use, *254*
Styrene (styrol), 246, 247, 248, 253, 254
Styrocamphene, 247, 248
Styrol, *see* Styrene
Styrolyl acetate, 356
Styrone, *see* Cinnamyl alcohol
Sumatra camphor, 262
"Surovo maslo," 13
"Syringa," 407
Syringa vulgaris, *338*

Tagetes glandulifera, *477*
Tagetes minuta, *477*
Tagetes oil, *477*
Tagetone, 480
Tanaceto, aceite esencial, *480*
Tanacetone, 477, 494
Tanacetum vulgare, *480*
Tanaise, essence de, *480*
Tansy—planting, cultivation and harvest, *481*
Tansy oil, *480*
Tansy oil—chemical composition, *484*
Tansy oil—physicochemical properties, *482*
Tansy oil—use, *485*
Tarragon oil, *459*
"Temol lawak," 123
Teresantalic acid, 186
Teresantalol, 185
Terpin hydrate, 98, 143
Terpinene, 100, 487
α-Terpinene, 430
α-Terpinenol, 487
β-Terpinenol, 487
1-Terpinen-4-ol, 77, 78, 100, 154
1-Terpinen-4-yl acetate, 100
1-Terpinen-4-yl formate, 100
Terpineol, 78, 227, 356, 458
α-Terpineol, 77, 98, 100, 231, 263, 310, 335, 374, 487
Terpinyl acetate, 98, 458
trans-Tetrahydrocadinene, 219
Tetrahydro-Δ^3-*p*-toluic aldehyde, 226
"Tjekoer" (*Kaempferia galanga*), 130
Thujone, 474, 482, 483, 484, 490, 491, 493, 494, 496
α-Thujone, 494
β-Thujone, 484, 494
Thujyl acetate, 493, 495
Thujyl alcohol, 484, 490, 493, 494, 495, 496
Thujyl isovalerate, 495
Thujyl palmitate, 495
Thymohydroquinone dimethyl ether, 428
Tiglic acid, 437
Tilia cordata, 421
Tilia platyphyllos, 421
Tilia tomentosa, 421
Tiliaceae oils, *419*
Tolu balsam, *see* Balsam Tolu
"Tolu-resin," 222
Tolu resinoid, *224*
Tolu-resinotannol, 223
p-Tolylmethylcarbinol, 123, 124
Triacontane, 437, 445
Trimyristin (glyceryl myristate), 71
"Tuberone," 347
Tuberose—botany, 343
Tuberose—*enfleurage*, *345*
Tuberose—extraction, *344*
Tuberose, concrete and absolute, *343*
Tuberose, concrete and absolute—absolute of *enfleurage*, *345*
Tuberose, concrete and absolute—absolute of extraction, 346
Tuberose, concrete and absolute—chemical composition, *347*
Tuberose, concrete and absolute—concrete of extraction, *346*
Tuberose, concrete and absolute—use, *348*
Turmerol, 121
Turmerone, 122
ar-Turmerone, 122

Umbelliferone methyl ether, 445

Valeraldehyde, 425
Valeric acid, 309, 470
Vanillin, 56, 218, 222, 247, 249, 254
Viola odorata, *391*
Violaceae oils, *389*
Violet, concrete and absolute, *391*
Violet, Parma, 391, 394, 395
Violet, Victoria, 392, 393, 395, 396
Violet flower oil—chemical composition, *394*
Violet flowers, concrete and absolute, *393*
Violet leaf, concrete and absolute, *396*
"Violet leaf alcohol" (2,6-nonadien-1-ol), 395, 397
"Violet leaf aldehyde" (2,6-nonadien-1-al), 395, 397
Violet leaf oil, 397

Digitized by Google
Original from CORNELL UNIVERSITY

Wermutöl, *487*
Witch Hazel oil, *255*
Wistaria, concrete and absolute, *240*
Wistaria senensis, *240*
"Wood oil," 259
"Woodwaxen," 239
Wormseed, Levant, 485
Wormseed, Levant, oil, *485*
Wormwood—botany, *487*
Wormwood—distillation, *489*
Wormwood, Roman, 487
Wormwood oil, *487*
Wormwood oil—chemical composition, *494*
Wormwood oil—physicochemical properties, *490*
Wormwood oil—use, *496*

Yarrow oil, *472*
Ylang ylang—botany, *278*
Ylang ylang—distillation, *281*, *289*, *303*
Ylang ylang—planting, cultivating, and harvesting, *279*, *303*
Ylang ylang, concrete and absolute, *312*
Ylang ylang, concrete and absolute—use, *315*
Ylang ylang oil, 267, *276*
Ylang ylang oil—chemical composition, *308*
Ylang ylang oil—physicochemical properties, *295*, *304*, 307
Ylang ylang oil—use, *315*
Ylang ylang oil, Albáy, 307
Ylang ylang oil, Nossi-Bé, Madagascar, Comoro Islands, *279*
Ylang ylang oil, Nossi-Bé, Madagascar, Comoro Islands—adulteration, *301*
Ylang ylang oil, Nossi-Bé, Madagascar, Comoro Islands—physicochemical properties, *295*
Ylang ylang oil, Nossi-Bé, Madagascar, Comoro Islands—quality, *293*
Ylang ylang oil, Nossi-Bé, Madagascar, Comoro Islands—total production, *300*
Ylang ylang oil, Nossi-Bé, Madagascar, Comoro Islands—yield, *293*
Ylang ylang oil, Philippines, *305*
Ylang ylang oil, Philippines—physicochemical properties, 307
Ylang ylang oil, Réunion Island, *302*
Ylang ylang oil, Réunion Island—physicochemical properties, *304*
Ylang ylang oil, terpeneless, *302*

"Zdravetz oil," 28
Zedoary oil, *125*
Zingerone (1-[4-hydroxy-3-methoxyphenyl]-3-butanone), 118, 119, 120
Zingiber mioga, 107
Zingiber nigrum, *105*
Zingiber officinale, *106*, 127
Zingiberaceae oils, *83*
Zingiberene, 116, *117*, 122, 126
Zingiberol, 118
Zitwerwurzelöl, 125
Zygophyllaceae oils, *195*

Digitized by Google
Original from CORNELL UNIVERSITY

Digitized by Google
Original from
CORNELL UNIVERSITY